Table 1: Geometry (Å) of ethylene.

| | X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 0.000000 | 0.669575 |
| C | 0.000000 | 0.000000 | -0.669575 |
| H | 0.000000 | 0.926294 | 1.235309 |
| H | 0.000000 | -0.926294 | 1.235309 |
| H | 0.000000 | 0.926294 | -1.235309 |
| H | 0.000000 | -0.926294 | -1.235309 |

Table 2: Geometry (Å) of isobutene.

| | X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 0.000000 | 1.463400 |
| C | 0.000000 | 0.000000 | 0.119614 |
| H | 0.000000 | 0.928447 | 2.027281 |
| H | 0.000000 | -0.928447 | 2.027281 |
| C | 0.000000 | 1.276163 | -0.680400 |
| H | 0.000000 | 2.156688 | -0.032951 |
| H | 0.881626 | 1.321381 | -1.330486 |
| H | -0.881626 | 1.321381 | -1.330486 |
| C | 0.000000 | -1.276163 | -0.680400 |
| H | 0.000000 | -2.156688 | -0.032951 |
| H | -0.881626 | -1.321381 | -1.330486 |
| H | 0.881626 | -1.321381 | -1.330486 |

Table 3: Geometry (Å) of trans-butadiene.

| | X | Y | Z |
|---|---|---|---|
| C | 0.608308 | 1.751027 | 0.000000 |
| C | 0.608308 | 0.403889 | 0.000000 |
| C | -0.608308 | -0.403889 | 0.000000 |
| C | -0.608308 | -1.751027 | 0.000000 |
| H | 1.533770 | 2.317122 | 0.000000 |
| H | -0.322818 | 2.311810 | 0.000000 |
| H | 1.556392 | -0.133780 | 0.000000 |
| H | -1.556392 | 0.133780 | 0.000000 |
| H | 0.322818 | -2.311810 | 0.000000 |
| H | -1.533770 | -2.317122 | 0.000000 |

Table 4: Geometry (Å) of formaldehyde.

| | X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 0.000000 | -0.533319 |
| O | 0.000000 | 0.000000 | 0.679545 |
| H | 0.000000 | 0.937366 | -1.118221 |
| H | 0.000000 | -0.937366 | -1.118221 |

Table 5: Geometry (Å) of acetaldehyde.

| | X | Y | Z |
|---|---|---|---|
| O | 1.212008 | 0.374458 | 0.000000 |
| C | 0.000000 | 0.462805 | 0.000000 |
| H | -0.486928 | 1.460337 | 0.000000 |
| C | -0.941279 | -0.711815 | 0.000000 |
| H | -0.384684 | -1.649523 | 0.000000 |
| H | -1.588387 | -0.656210 | 0.881703 |
| H | -1.588387 | -0.656210 | -0.881703 |

Table 6: Geometry (Å) of acetone.

| | X | Y | Z |
|---|---|---|---|
| O | 0.000000 | 0.000000 | 1.404559 |
| C | 0.000000 | 0.000000 | 0.184831 |
| C | 0.000000 | 1.286642 | -0.616357 |
| C | 0.000000 | -1.286642 | -0.616357 |
| H | 0.000000 | 2.145130 | 0.055418 |
| H | 0.000000 | -2.145130 | 0.055418 |
| H | -0.881514 | 1.320931 | -1.265003 |
| H | 0.881514 | 1.320931 | -1.265003 |
| H | 0.881514 | -1.320931 | -1.265003 |
| H | -0.881514 | -1.320931 | -1.265003 |

Table 7: Geometry (Å) of pyridine.

| | X | Y | Z |
|---|---|---|---|
| N | 0.000000 | 0.000000 | 1.428332 |
| C | 0.000000 | 0.000000 | -1.391651 |
| C | 0.000000 | 1.144923 | 0.723091 |
| C | 0.000000 | -1.144923 | 0.723091 |
| C | 0.000000 | -1.199476 | -0.674912 |
| C | 0.000000 | 1.199476 | -0.674912 |
| H | 0.000000 | 0.000000 | -2.478143 |
| H | 0.000000 | 2.061946 | 1.308643 |
| H | 0.000000 | -2.061946 | 1.308643 |
| H | 0.000000 | -2.159346 | -1.182856 |
| H | 0.000000 | 2.159346 | -1.182856 |

Table 8: Geometry (Å) of pyrazine.

| | X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 1.133849 | 0.699678 |
| C | 0.000000 | 1.133849 | -0.699678 |
| N | 0.000000 | 0.000000 | -1.420331 |
| C | 0.000000 | -1.133849 | -0.699678 |
| C | 0.000000 | -1.133849 | 0.699678 |
| N | 0.000000 | 0.000000 | 1.420331 |
| H | 0.000000 | 2.068862 | 1.254885 |
| H | 0.000000 | 2.068862 | -1.254885 |
| H | 0.000000 | -2.068862 | -1.254885 |
| H | 0.000000 | -2.068862 | 1.254885 |

Table 9: Geometry (Å) of pyrimidine.

| | X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 0.000000 | -1.312458 |
| N | 0.000000 | 1.203128 | -0.717845 |
| C | 0.000000 | 1.188178 | 0.625296 |
| C | 0.000000 | 0.000000 | 1.356430 |
| C | 0.000000 | -1.188178 | 0.625296 |
| N | 0.000000 | -1.203128 | -0.717845 |
| H | 0.000000 | 2.156668 | 1.120301 |
| H | 0.000000 | 0.000000 | -2.399286 |
| H | 0.000000 | 0.000000 | 2.441125 |
| H | 0.000000 | -2.156668 | 1.120301 |

Table 10: Geometry (Å) of pyridazine.

| | X | Y | Z |
|---|---|---|---|
| N | 0.000000 | 0.670782 | -1.238620 |
| C | 0.000000 | 1.325351 | -0.064846 |
| C | 0.000000 | 0.694555 | 1.184924 |
| C | 0.000000 | -0.694555 | 1.184924 |
| C | 0.000000 | -1.325351 | -0.064846 |
| N | 0.000000 | -0.670782 | -1.238620 |
| H | 0.000000 | 1.274441 | 2.102771 |
| H | 0.000000 | 2.408352 | -0.152902 |
| H | 0.000000 | -1.274441 | 2.102771 |
| H | 0.000000 | -2.408352 | -0.152902 |

Table 11: Geometry (Å) of S-tetrazine

| | X | Y | Z |
|---|---|---|---|
| C | 0.000000 | 0.000000 | 1.265707 |
| N | 0.000000 | 1.203065 | -0.667089 |
| C | 0.000000 | 0.000000 | -1.265707 |
| N | 0.000000 | -1.203065 | 0.667089 |
| H | 0.000000 | 0.000000 | 2.350926 |
| H | 0.000000 | 0.000000 | -2.350926 |
| N | 0.000000 | -1.203065 | -0.667089 |
| N | 0.000000 | 1.203065 | 0.667089 |

Table 12: Calculated and experimental transition energies (eV) for ethylene. The reference for the experimental data are reported in the text.

| | $1B_{3u}$ Ryd | $1B_{1u}$ $\pi \rightarrow \pi^*$ | $1B_{1g}$ Ryd | $1B_{2g}$ Ryd | $2A_g$ Ryd | $2B_{3u}$ Ryd | $3B_{3u}$ Ryd | $4B_{3u}$ Ryd | $3B_{1g}$ Ryd | $2B_{1u}$ Ryd | $5B_{3u}$ Ryd |
|---|---|---|---|---|---|---|---|---|---|---|---|
| RPA | 7.08 | 7.36 | 7.67 | 7.83 | 8.04 | 8.57 | 8.81 | 8.90 | 9.23 | 8.95 | 9.35 |
| CIS | 7.10 | 7.70 | 7.68 | 7.83 | 8.07 | 8.57 | 8.81 | 8.90 | 9.28 | 8.98 | 9.35 |
| CIS(D) | 7.17 | 8.01 | 7.81 | 7.82 | 8.14 | 8.61 | 8.85 | 8.94 | 8.80 | 9.02 | 9.35 |
| LSDA | 6.80 | 7.48 | 7.32 | 7.31 | 7.52 | 7.49 | 7.71 | 7.87 | 7.57 | 7.75 | 8.32 |
| BLYP | 6.14 | 6.86 | 6.55 | 6.51 | 6.69 | 6.65 | 6.85 | 7.08 | 7.18 | 7.16 | 7.50 |
| OLYP | 5.93 | 6.85 | 6.41 | 6.36 | 6.65 | 6.67 | 6.88 | 7.05 | 7.16 | 7.11 | 7.39 |
| BP86 | 6.48 | 7.11 | 6.86 | 6.82 | 6.97 | 6.95 | 7.14 | 7.38 | 7.52 | 7.36 | 7.78 |
| BVP86 | 6.48 | 7.11 | 6.85 | 6.81 | 6.96 | 6.94 | 7.13 | 7.37 | 7.51 | 7.36 | 7.78 |
| PBEPBE | 6.38 | 7.07 | 6.79 | 6.77 | 6.92 | 6.86 | 7.08 | 7.29 | 7.41 | 7.33 | 7.78 |
| HCTH | 6.49 | 7.23 | 6.96 | 6.97 | 7.10 | 7.00 | 7.27 | 7.46 | 7.53 | 7.39 | 8.06 |
| THCTH | 6.42 | 7.15 | 6.87 | 6.85 | 7.01 | 6.94 | 7.17 | 7.37 | 7.47 | 7.32 | 7.89 |
| BB95 | 6.28 | 6.87 | 6.61 | 6.58 | 6.72 | 6.67 | 6.87 | 7.13 | 7.24 | 7.25 | 7.58 |
| VSXC | 6.59 | 7.10 | 6.85 | 6.85 | 6.97 | 6.89 | 7.11 | 7.36 | 7.51 | 7.48 | 7.99 |
| TPSSTPSS | 6.42 | 7.05 | 6.78 | 6.77 | 6.89 | 6.85 | 7.06 | 7.29 | 7.41 | 7.38 | 7.78 |
| O3LYP | 6.22 | 7.18 | 6.74 | 6.70 | 7.01 | 7.12 | 7.30 | 7.45 | 7.59 | 7.41 | 7.75 |
| B3LYP | 6.56 | 7.32 | 7.07 | 7.07 | 7.33 | 7.45 | 7.61 | 7.77 | 7.90 | 7.69 | 8.09 |
| B3P86 | 7.03 | 7.51 | 7.58 | 7.57 | 7.86 | 8.04 | 8.19 | 8.33 | 8.15 | 8.24 | 8.62 |
| B3VP86 | 6.82 | 7.44 | 7.30 | 7.29 | 7.50 | 7.60 | 7.77 | 7.95 | 8.00 | 7.81 | 8.27 |
| PBE1PBE | 6.80 | 7.46 | 7.32 | 7.33 | 7.54 | 7.66 | 7.83 | 7.98 | 8.06 | 7.88 | 8.35 |
| B1B95 | 6.72 | 7.41 | 7.19 | 7.19 | 7.38 | 7.49 | 7.64 | 7.83 | 7.93 | 7.71 | 8.17 |
| THCTHHYB | 6.73 | 7.39 | 7.21 | 7.20 | 7.36 | 7.38 | 7.58 | 7.76 | 7.88 | 7.62 | 8.20 |
| TPSSh | 6.60 | 7.32 | 7.04 | 7.02 | 7.16 | 7.17 | 7.37 | 7.57 | 7.69 | 7.50 | 8.01 |
| M05 | 6.64 | 7.20 | 7.22 | 7.24 | 7.48 | 7.61 | 7.80 | 7.93 | 7.90 | 7.83 | 8.33 |
| BH&H | 6.97 | 7.49 | 7.55 | 7.61 | 7.90 | 8.17 | 8.32 | 8.47 | 8.33 | 8.41 | 8.75 |
| BH&HLYP | 6.90 | 7.42 | 7.46 | 7.51 | 7.82 | 8.15 | 8.29 | 8.43 | 8.48 | 8.41 | 8.70 |
| BMK | 7.11 | 7.59 | 7.59 | 7.62 | 7.82 | 8.11 | 8.22 | 8.39 | 8.25 | 8.29 | 8.67 |
| M05-2X | 7.42 | 7.53 | 7.97 | 8.11 | 8.33 | 8.54 | 8.73 | 8.87 | 8.70 | 8.77 | 9.20 |
| HSE1PBE | 6.84 | 7.46 | 7.37 | 7.37 | 7.57 | 7.56 | 7.78 | 7.95 | 8.03 | 7.81 | 8.38 |
| CAM-B3LYP | 6.89 | 7.44 | 7.48 | 7.54 | 7.87 | 8.26 | 8.43 | 8.55 | 8.53 | 8.58 | 8.85 |
| LC-BLYP | 7.41 | 7.56 | 8.04 | 8.21 | 8.52 | 8.99 | 9.27 | 9.43 | 9.53 | 9.50 | 9.90 |
| LC-$\omega$PBE | 7.52 | 7.63 | 8.12 | 8.27 | 8.49 | 8.99 | 9.23 | 9.33 | 9.44 | 9.38 | 9.79 |
| EOM-CCSD | 7.28 | 8.12 | 7.93 | 7.96 | 8.31 | 8.80 | 9.06 | 9.16 | 9.28 | 9.28 | 9.62 |
| Exp. | 7.11 | 7.65 | 7.80 | 7.90 | 8.28 | 8.62 | 8.90 | 9.08 | 9.20 | 9.33 | 9.51 |

Table 13: Calculated and experimental transition energies (eV) for isobutene. The reference for the experimental data are reported in the text. The SCF of BB95 and B1B95 did not converge.

| | $B_1$ Ryd | $A_1$ Ryd |
|---|---|---|
| RPA | 6.55 | 6.84 |
| CIS | 6.56 | 6.98 |
| CIS(D) | 6.27 | 6.84 |
| LSDA | 5.63 | 6.28 |
| BLYP | 5.14 | 5.69 |
| OLYP | 4.90 | 5.53 |
| BP86 | 5.49 | 5.98 |
| BVP86 | 5.48 | 5.97 |
| PBEPBE | 5.33 | 5.91 |
| HCTH | 5.37 | 6.04 |
| THCTH | 5.38 | 6.00 |
| BB95 | | |
| VSXC | 5.55 | 6.05 |
| TPSSTPSS | 5.46 | 5.96 |
| O3LYP | 5.26 | 5.88 |
| B3LYP | 5.66 | 6.23 |
| B3P86 | 6.10 | 6.61 |
| B3VP86 | 5.92 | 6.41 |
| PBE1PBE | 5.90 | 6.42 |
| B1B95 | | |
| THCTHHYB | 5.80 | 6.32 |
| TPSSh | 5.68 | 6.19 |
| M05 | 5.76 | 6.28 |
| BH&H | 6.16 | 6.65 |
| BH&HLYP | 6.15 | 6.63 |
| BMK | 6.32 | 6.70 |
| M05-2X | 6.63 | 6.91 |
| HSE1PBE | 5.91 | 6.44 |
| CAM-B3LYP | 6.12 | 6.59 |
| LC-BLYP | 6.71 | 6.95 |
| LC-$\omega$PBE | 6.82 | 7.00 |
| EOM-CCSD | 6.40 | 6.96 |
| Exp. | 6.17 | $\sim$6.70 |

Table 14: Calculated and experimental transition energies (eV) for trans-1,3-butadiene. The reference for the experimental data are reported in the text.

| | $1B_u$ $\pi \rightarrow \pi^*$ | $1B_g$ Ryd | $2A_u$ Ryd | $2B_u$ Ryd | $2B_g$ Ryd | $3A_g$ Ryd | $3B_u$ Ryd |
|---|---|---|---|---|---|---|---|
| RPA | 5.89 | 6.10 | 6.43 | 6.88 | 7.20 | 7.40 | 7.74 |
| CIS | 6.16 | 6.11 | 6.44 | 6.96 | 7.20 | 7.40 | 7.75 |
| CIS(D) | 6.25 | 6.12 | 6.43 | 7.00 | 7.17 | 7.40 | 7.71 |
| LSDA | 5.48 | 5.89 | 6.13 | 6.62 | 6.58 | 6.80 | 6.93 |
| BLYP | 5.31 | 5.22 | 5.46 | 5.83 | 5.73 | 5.97 | 6.09 |
| OLYP | 5.27 | 4.99 | 5.23 | 5.81 | 5.73 | 5.95 | 6.07 |
| BP86 | 5.43 | 5.58 | 5.81 | 6.08 | 6.05 | 6.25 | 6.39 |
| BVP86 | 5.42 | 5.58 | 5.81 | 6.08 | 6.05 | 6.25 | 6.39 |
| PBEPBE | 5.41 | 5.46 | 5.73 | 6.03 | 5.95 | 6.17 | 6.31 |
| HCTH | 5.42 | 5.55 | 5.79 | 6.20 | 6.08 | 6.34 | 6.47 |
| THCTH | 5.39 | 5.51 | 5.80 | 6.12 | 6.03 | 6.27 | 6.40 |
| BB95 | 5.37 | 5.39 | 5.61 | 5.86 | 5.77 | 6.00 | 6.13 |
| VSXC | 5.55 | 5.68 | 5.87 | 6.07 | 5.95 | 6.19 | 6.33 |
| TPSSTPSS | 5.48 | 5.49 | 5.74 | 5.99 | 5.91 | 6.13 | 6.26 |
| O3LYP | 5.43 | 5.28 | 5.59 | 6.10 | 6.12 | 6.30 | 6.43 |
| B3LYP | 5.54 | 5.63 | 5.88 | 6.36 | 6.41 | 6.59 | 6.74 |
| B3P86 | 5.64 | 6.12 | 6.37 | 6.87 | 7.00 | 7.17 | 7.33 |
| B3VP86 | 5.61 | 5.89 | 6.14 | 6.52 | 6.59 | 6.75 | 6.91 |
| PBE1PBE | 5.65 | 5.87 | 6.12 | 6.54 | 6.60 | 6.77 | 6.91 |
| B1B95 | 5.61 | 5.79 | 6.04 | 6.39 | 6.45 | 6.60 | 6.77 |
| THCTHHYB | 5.55 | 5.81 | 6.11 | 6.39 | 6.39 | 6.57 | 6.72 |
| TPSSh | 5.57 | 5.65 | 5.94 | 6.21 | 6.18 | 6.37 | 6.51 |
| M05 | 5.47 | 5.75 | 6.11 | 6.50 | 6.57 | 6.75 | 6.88 |
| BH&H | 5.79 | 6.03 | 6.42 | 6.82 | 6.98 | 7.15 | 7.32 |
| BH&HLYP | 5.75 | 5.95 | 6.34 | 6.75 | 6.93 | 7.11 | 7.30 |
| BMK | 5.81 | 6.14 | 6.47 | 6.74 | 6.94 | 7.05 | 7.25 |
| M05-2X | 5.80 | 6.52 | 6.93 | 7.25 | 7.40 | 7.56 | 7.72 |
| HSE1PBE | 5.64 | 5.89 | 6.21 | 6.55 | 6.50 | 6.73 | 6.85 |
| CAM-B3LYP | 5.73 | 5.99 | 6.41 | 6.83 | 7.04 | 7.26 | 7.49 |
| LC-BLYP | 5.96 | 6.52 | 6.82 | 7.41 | 7.72 | 8.01 | 8.38 |
| LC-$\omega$PBE | 5.97 | 6.64 | 6.94 | 7.40 | 7.75 | 7.96 | 8.30 |
| EOM-CCSD | 6.39 | 6.24 | 6.70 | 7.17 | 7.35 | 7.62 | 7.97 |
| Exp. | 5.91 | 6.22 | 6.66 | 7.07 | 7.36 | 7.62 | 8.00 |

Table 15: Calculated and experimental transition energies (eV) for formaldehyde. The reference for the experimental data are reported in the text.

| | $1A_2$ $n \rightarrow \pi^*$ | $1B_2$ Ryd | $2B_2$ Ryd | $2A_1$ Ryd | $2A_2$ Ryd | $3B_2$ Ryd | $1B_1$ $\pi \rightarrow \pi^*$ | $3A_2$ Ryd | $4B_2$ Ryd | $4A_1$ Ryd | $5B_2$ Ryd |
|---|---|---|---|---|---|---|---|---|---|---|---|
| RPA | 4.34 | 8.59 | 9.33 | 9.18 | 9.74 | 10.47 | 9.51 | 10.69 | 10.62 | 10.67 | 10.68 |
| CIS | 4.52 | 8.60 | 9.34 | 9.48 | 9.75 | 10.47 | 9.76 | 10.70 | 10.63 | 10.70 | 10.68 |
| CIS(D) | 4.03 | 6.43 | 7.26 | 8.02 | 7.49 | 8.13 | 9.43 | 8.62 | 8.28 | 8.42 | 8.31 |
| LSDA | 3.68 | 6.10 | 6.88 | 6.81 | 6.94 | 6.90 | 8.79 | 7.35 | 7.19 | 7.32 | 7.26 |
| BLYP | 3.80 | 5.63 | 6.26 | 6.20 | 6.29 | 6.29 | 8.78 | 6.73 | 6.59 | 6.71 | 6.67 |
| OLYP | 3.84 | 5.37 | 6.15 | 6.08 | 6.26 | 6.26 | 8.87 | 6.62 | 6.51 | 6.66 | 6.63 |
| BP86 | 3.81 | 5.88 | 6.45 | 6.39 | 6.50 | 6.46 | 8.84 | 6.93 | 6.80 | 6.81 | 6.86 |
| BVP86 | 3.82 | 5.89 | 6.45 | 6.39 | 6.50 | 6.46 | 8.85 | 6.94 | 6.80 | 6.80 | 6.86 |
| PBEPBE | 3.78 | 5.76 | 6.36 | 6.33 | 6.42 | 6.40 | 8.83 | 6.86 | 6.71 | 6.81 | 6.76 |
| HCTH | 3.86 | 5.94 | 6.60 | 6.61 | 6.71 | 6.69 | 8.91 | 7.18 | 6.97 | 7.06 | 7.01 |
| THCTH | 3.93 | 5.96 | 6.63 | 6.60 | 6.70 | 6.68 | 8.90 | 7.15 | 6.97 | 7.08 | 7.02 |
| BB95 | 3.72 | 5.66 | 6.10 | 6.12 | 6.21 | 6.17 | 8.71 | 6.67 | 6.49 | 6.51 | 6.56 |
| VSXC | 4.03 | 6.09 | 6.48 | 6.48 | 6.57 | 6.58 | 9.09 | 7.12 | 6.88 | 6.98 | 7.03 |
| TPSSTPSS | 4.02 | 5.95 | 6.49 | 6.46 | 6.55 | 6.54 | 9.01 | 7.00 | 6.86 | 6.94 | 6.90 |
| O3LYP | 3.89 | 5.91 | 6.69 | 6.66 | 6.86 | 6.95 | 8.97 | 7.25 | 7.16 | 7.32 | 7.29 |
| B3LYP | 3.89 | 6.46 | 7.22 | 7.19 | 7.37 | 7.46 | 8.96 | 7.79 | 7.68 | 7.83 | 7.81 |
| B3P86 | 3.91 | 6.87 | 7.66 | 7.63 | 7.85 | 7.99 | 9.02 | 8.30 | 8.23 | 8.37 | 8.32 |
| B3VP86 | 3.90 | 6.65 | 7.36 | 7.32 | 7.46 | 7.55 | 9.01 | 7.89 | 7.80 | 7.93 | 7.90 |
| PBE1PBE | 3.90 | 6.70 | 7.43 | 7.42 | 7.57 | 7.67 | 9.05 | 7.99 | 7.89 | 8.03 | 8.01 |
| B1B95 | 3.83 | 6.59 | 7.27 | 7.24 | 7.36 | 7.49 | 8.92 | 7.82 | 7.71 | 7.80 | 7.83 |
| THCTHHYB | 3.92 | 6.52 | 7.22 | 7.18 | 7.28 | 7.29 | 8.98 | 7.69 | 7.56 | 7.69 | 7.64 |
| TPSSh | 4.05 | 6.32 | 6.98 | 6.92 | 7.02 | 7.01 | 9.08 | 7.43 | 7.31 | 7.42 | 7.38 |
| M05 | 3.84 | 6.46 | 7.29 | 7.27 | 7.49 | 7.59 | 8.79 | 7.90 | 7.78 | 7.94 | 7.92 |
| BH&H | 3.91 | 7.35 | 8.09 | 8.20 | 8.39 | 8.71 | 9.17 | 8.98 | 8.89 | 8.98 | 9.03 |
| BH&HLYP | 4.04 | 7.43 | 8.18 | 8.27 | 8.50 | 8.87 | 9.19 | 9.13 | 9.06 | 9.07 | 9.16 |
| BMK | 3.84 | 7.27 | 7.91 | 7.94 | 8.06 | 8.37 | 9.01 | 8.61 | 8.56 | 8.61 | 8.65 |
| M05-2X | 3.64 | 7.70 | 8.45 | 8.56 | 8.76 | 9.02 | 8.86 | 9.30 | 9.19 | 9.30 | 9.35 |
| HSE1PBE | 3.90 | 6.74 | 7.49 | 7.47 | 7.61 | 7.58 | 9.04 | 7.98 | 7.83 | 8.00 | 7.94 |
| CAM-B3LYP | 3.88 | 6.88 | 7.63 | 7.73 | 7.94 | 8.47 | 9.05 | 8.75 | 8.65 | 8.71 | 8.73 |
| LC-BLYP | 3.86 | 7.41 | 8.19 | 8.35 | 8.55 | 9.34 | 9.17 | 9.67 | 9.53 | 9.78 | 9.62 |
| LC-$\omega$PBE | 3.88 | 7.30 | 8.05 | 8.15 | 8.31 | 9.04 | 9.16 | 9.32 | 9.20 | 9.46 | 9.30 |
| EOM-CCSD | 3.99 | 7.04 | 7.87 | 7.98 | 8.20 | 8.94 | 9.33 | 9.27 | 9.13 | 9.37 | 9.18 |
| Exp. | 4.00 | 7.08 | 7.97 | 8.14 | 8.37 | 8.88 | 9.00 | 9.22 | 9.26 | 9.58 | 9.63 |

Table 16: Calculated and experimental transition energies (eV) for acetaldehyde. The reference for the experimental data are reported in the text. The SCF of BB95 and B1B95 did not converge.

| | A" | 2A' | 3A' | 4A' | 6A' | 7A' |
|---|---|---|---|---|---|---|
| | $n \rightarrow \pi^*$ | Ryd | Ryd | Ryd | Ryd | Ryd |
| RPA | 4.75 | 8.45 | 9.10 | 9.19 | 10.04 | 10.12 |
| CIS | 4.92 | 8.46 | 9.17 | 9.27 | 10.04 | 10.17 |
| CIS(D) | 4.33 | 6.14 | 6.84 | 7.37 | 7.54 | 7.85 |
| LSDA | 4.05 | 5.75 | 6.28 | 6.59 | 6.69 | 6.77 |
| BLYP | 4.13 | 5.31 | 5.73 | 5.91 | 6.00 | 6.09 |
| OLYP | 4.18 | 5.03 | 5.52 | 5.81 | 6.00 | 6.06 |
| BP86 | 4.13 | 5.59 | 5.97 | 6.13 | 6.24 | 6.29 |
| BVP86 | 4.13 | 5.60 | 5.97 | 6.13 | 6.24 | 6.29 |
| PBEPBE | 4.11 | 5.43 | 5.88 | 6.05 | 6.12 | 6.22 |
| HCTH | 4.19 | 5.55 | 6.07 | 6.28 | 6.35 | 6.48 |
| THCTH | 4.23 | 5.60 | 6.09 | 6.32 | 6.39 | 6.47 |
| BB95 | | | | | | |
| VSXC | 4.40 | 5.79 | 6.15 | 6.19 | 6.31 | 6.40 |
| TPSSTPSS | 4.30 | 5.60 | 6.02 | 6.14 | 6.23 | 6.32 |
| O3LYP | 4.23 | 5.60 | 6.10 | 6.39 | 6.69 | 6.74 |
| B3LYP | 4.23 | 6.20 | 6.69 | 6.95 | 7.21 | 7.26 |
| B3P86 | 4.24 | 6.61 | 7.11 | 7.40 | 7.77 | 7.79 |
| B3VP86 | 4.23 | 6.40 | 6.85 | 7.08 | 7.33 | 7.37 |
| PBE1PBE | 4.24 | 6.45 | 6.95 | 7.17 | 7.45 | 7.49 |
| B1B95 | | | | | | |
| THCTHHYB | 4.24 | 6.23 | 6.70 | 6.91 | 7.05 | 7.11 |
| TPSSh | 4.34 | 6.00 | 6.45 | 6.63 | 6.75 | 6.82 |
| M05 | 4.21 | 6.23 | 6.78 | 7.06 | 7.36 | 7.41 |
| BH&H | 4.32 | 7.16 | 7.77 | 7.96 | 8.50 | 8.53 |
| BH&HLYP | 4.41 | 7.23 | 7.82 | 8.02 | 8.59 | 8.63 |
| BMK | 4.16 | 7.06 | 7.52 | 7.68 | 8.11 | 8.13 |
| M05-2X | 3.98 | 7.50 | 8.13 | 8.32 | 8.79 | 8.81 |
| HSE1PBE | 4.24 | 6.46 | 6.97 | 7.20 | 7.31 | 7.38 |
| CAM-B3LYP | 4.24 | 6.72 | 7.33 | 7.54 | 8.17 | 8.25 |
| LC-BLYP | 4.24 | 7.32 | 8.06 | 8.28 | 9.05 | 9.20 |
| LC-$\omega$PBE | 4.22 | 7.21 | 7.88 | 8.09 | 8.78 | 8.88 |
| EOM-CCSD | 4.32 | 6.80 | 7.48 | 7.70 | 8.41 | 8.54 |
| Exp. | 4.28 | 6.82 | 7.46 | 7.75 | 8.43 | 8.69 |

Table 17: Calculated and experimental transition energies (eV) for acetone. The reference for the experimental data are reported in the text.

| | $1A_2$ $n \rightarrow \pi^*$ | $1B_2$ Ryd | $2A_2$ Ryd | $2A_1$ Ryd | $2B_2$ Ryd | $3A_1$ Ryd | $3B_2$ Ryd | $1B_1$ Ryd |
|---|---|---|---|---|---|---|---|---|
| RPA | 5.00 | 8.25 | 9.05 | 9.10 | 9.16 | 9.46 | 9.61 | 9.67 |
| CIS | 5.16 | 8.26 | 9.06 | 9.18 | 9.16 | 9.74 | 9.61 | 9.87 |
| CIS(D) | 4.45 | 5.70 | 6.48 | 6.78 | 6.52 | 8.38 | 6.90 | 7.34 |
| LSDA | 4.19 | 5.25 | 6.24 | 6.11 | 6.30 | 6.44 | 6.34 | 6.49 |
| BLYP | 4.20 | 4.82 | 5.57 | 5.46 | 5.58 | 5.70 | 5.60 | 5.72 |
| OLYP | 4.23 | 4.53 | 5.42 | 5.27 | 5.49 | 5.70 | 5.61 | 5.75 |
| BP86 | 4.22 | 5.15 | 5.79 | 5.74 | 5.82 | 5.95 | 5.85 | 5.93 |
| BVP86 | 4.23 | 5.15 | 5.79 | 5.74 | 5.82 | 5.95 | 5.85 | 5.93 |
| PBEPBE | 4.20 | 4.94 | 5.72 | 5.65 | 5.75 | 5.86 | 5.78 | 5.89 |
| HCTH | 4.27 | 5.02 | 5.98 | 5.89 | 5.98 | 6.08 | 6.02 | 6.12 |
| THCTH | 4.31 | 5.10 | 5.97 | 5.88 | 6.01 | 6.10 | 6.02 | 6.15 |
| BB95 | 4.11 | 4.81 | 5.52 | 5.49 | 5.23 | 5.63 | 5.57 | 5.75 |
| VSXC | 4.53 | 5.33 | 5.95 | 5.93 | 5.92 | 6.07 | 5.98 | 6.06 |
| TPSSTPSS | 4.35 | 5.13 | 5.81 | 5.75 | 5.83 | 5.95 | 5.86 | 5.96 |
| O3LYP | 4.32 | 5.14 | 6.01 | 5.91 | 6.09 | 6.40 | 6.29 | 6.44 |
| B3LYP | 4.36 | 5.76 | 6.61 | 6.52 | 6.66 | 6.93 | 6.80 | 6.95 |
| B3P86 | 4.38 | 6.19 | 7.08 | 6.99 | 7.15 | 7.52 | 7.34 | 7.49 |
| B3VP86 | 4.37 | 6.00 | 6.76 | 6.70 | 6.82 | 7.08 | 6.94 | 7.05 |
| PBE1PBE | 4.39 | 6.04 | 6.85 | 6.80 | 6.90 | 7.19 | 7.05 | 7.21 |
| B1B95 | 4.29 | 6.07 | 7.16 | 6.97 | 7.37 | 7.82 | 7.69 | 8.07 |
| THCTHHYB | 4.36 | 5.80 | 6.56 | 6.51 | 6.64 | 6.78 | 6.66 | 6.80 |
| TPSSh | 4.42 | 5.56 | 6.27 | 6.21 | 6.32 | 6.47 | 6.36 | 6.49 |
| M05 | 4.36 | 5.82 | 6.75 | 6.69 | 6.79 | 7.11 | 6.96 | 7.14 |
| BH&H | 4.54 | 6.82 | 7.71 | 7.72 | 7.77 | 8.25 | 8.05 | 8.28 |
| BH&HLYP | 4.59 | 6.89 | 7.76 | 7.74 | 7.80 | 8.30 | 8.12 | 8.35 |
| BMK | 4.30 | 6.72 | 7.35 | 7.35 | 7.42 | 7.81 | 7.68 | 7.82 |
| M05-2X | 4.14 | 7.16 | 8.11 | 8.10 | 8.14 | 8.54 | 8.34 | 8.57 |
| HSE1PBE | 4.39 | 6.04 | 6.87 | 6.80 | 6.91 | 7.05 | 6.96 | 7.09 |
| CAM-B3LYP | 4.42 | 6.39 | 7.29 | 7.32 | 7.34 | 7.90 | 7.70 | 7.97 |
| LC-BLYP | 4.46 | 7.11 | 8.07 | 8.21 | 8.17 | 8.86 | 8.59 | 8.97 |
| LC-$\omega$PBE | 4.40 | 7.02 | 7.84 | 7.98 | 7.93 | 8.57 | 8.35 | 8.64 |
| EOM-CCSD | 4.47 | 6.40 | 7.29 | 7.39 | 7.37 | 8.00 | 7.79 | 8.07 |
| Exp. | 4.43 | 6.36 | 7.36 | 7.41 | 7.49 | 7.8 | 8.09 | 8.17 |

Table 18: Calculated and experimental transition energies (eV) for pyridine. The reference for the experimental data are reported in the text. The SCF of BB95 and B1B95 did not converge.

| | $B_1$ | $B_2$ | $A_2$ | $A_1$ |
|---|---|---|---|---|
| | $n \rightarrow \pi^*$ | $\pi \rightarrow \pi^*$ | $n \rightarrow \pi^*$ | $\pi \rightarrow \pi^*$ |
| RPA | 5.95 | 5.85 | 7.33 | 6.09 |
| CIS | 6.13 | 6.10 | 7.41 | 6.42 |
| CIS(D) | 5.30 | 5.35 | 5.38 | 6.90 |
| LSDA | 4.24 | 5.33 | 4.31 | 6.19 |
| BLYP | 4.37 | 5.26 | 4.47 | 6.07 |
| OLYP | 4.42 | 5.30 | 4.53 | 6.13 |
| BP86 | 4.37 | 5.31 | 4.46 | 6.14 |
| BVP86 | 4.36 | 5.31 | 4.47 | 6.14 |
| PBEPBE | 4.34 | 5.31 | 4.44 | 6.17 |
| HCTH | 4.43 | 5.31 | 4.54 | 6.12 |
| THCTH | 4.47 | 5.29 | 4.61 | 6.06 |
| BB95 | | | | |
| VSXC | 4.62 | 5.48 | 4.77 | 6.24 |
| TPSSTPSS | 4.56 | 5.39 | 4.71 | 6.19 |
| O3LYP | 4.65 | 5.40 | 4.88 | 6.24 |
| B3LYP | 4.78 | 5.44 | 5.10 | 6.23 |
| B3P86 | 4.79 | 5.48 | 5.10 | 6.29 |
| B3VP86 | 4.78 | 5.48 | 5.08 | 6.28 |
| PBE1PBE | 4.85 | 5.53 | 5.21 | 6.33 |
| B1B95 | | | | |
| THCTHHYB | 4.71 | 5.44 | 4.97 | 6.23 |
| TPSSh | 4.75 | 5.47 | 5.00 | 6.26 |
| M05 | 4.68 | 5.40 | 4.97 | 6.03 |
| BH&H | 5.19 | 5.69 | 5.87 | 6.39 |
| BH&HLYP | 5.29 | 5.65 | 6.00 | 6.29 |
| BMK | 4.94 | 5.67 | 5.46 | 6.50 |
| M05-2X | 4.92 | 5.68 | 5.59 | 6.47 |
| HSE1PBE | 4.84 | 5.52 | 5.19 | 6.31 |
| CAM-B3LYP | 5.05 | 5.52 | 5.46 | 6.34 |
| LC-BLYP | 5.30 | 5.58 | 5.84 | 6.43 |
| LC-$\omega$PBE | 5.20 | 5.56 | 5.63 | 6.48 |
| EOM-CCSD | 5.22 | 5.24 | 5.67 | 6.77 |
| Exp. | 4.59 | 4.99 | 5.43 | 6.38 |

Table 19: Calculated and experimental transition energies (eV) for pyrazine. The reference for the experimental data are reported in the text.

| | $B_{3u}$ $n \rightarrow \pi^*$ | $B_{2u}$ $\pi \rightarrow \pi^*$ | $B_{2g}$ $n \rightarrow \pi^*$ | $B_{1g}$ $n \rightarrow \pi^*$ | $B_{1u}$ $\pi \rightarrow \pi^*$ |
|---|---|---|---|---|---|
| RPA | 4.93 | 5.56 | 6.52 | 9.73 | 6.20 |
| CIS | 5.12 | 5.88 | 6.72 | 9.77 | 6.57 |
| CIS(D) | 4.46 | 5.22 | 6.28 | 6.45 | 7.20 |
| LSDA | 3.45 | 5.24 | 5.00 | 5.42 | 6.41 |
| BLYP | 3.59 | 5.18 | 5.10 | 5.57 | 6.29 |
| OLYP | 3.62 | 5.20 | 5.19 | 5.68 | 6.33 |
| BP86 | 3.57 | 5.22 | 5.13 | 5.59 | 6.36 |
| BVP86 | 3.57 | 5.22 | 5.13 | 5.60 | 6.36 |
| PBEPBE | 3.55 | 5.22 | 5.11 | 5.57 | 6.36 |
| HCTH | 3.61 | 5.21 | 5.19 | 5.69 | 6.35 |
| THCTH | 3.66 | 5.18 | 5.22 | 5.76 | 6.29 |
| BB95 | 3.48 | 5.19 | 5.02 | 5.44 | 6.11 |
| VSXC | 3.78 | 5.35 | 5.41 | 5.97 | 6.47 |
| TPSSTPSS | 3.74 | 5.28 | 5.33 | 5.89 | 6.46 |
| O3LYP | 3.82 | 5.28 | 5.46 | 6.13 | 6.44 |
| B3LYP | 3.94 | 5.31 | 5.56 | 6.40 | 6.43 |
| B3P86 | 3.93 | 5.35 | 5.59 | 6.42 | 6.49 |
| B3VP86 | 3.93 | 5.34 | 5.59 | 6.41 | 6.48 |
| PBE1PBE | 3.99 | 5.38 | 5.68 | 6.60 | 6.53 |
| B1B95 | 3.91 | 5.35 | 5.58 | 6.47 | 6.51 |
| THCTHHYB | 3.87 | 5.31 | 5.51 | 6.26 | 6.43 |
| TPSSh | 3.90 | 5.33 | 5.56 | 6.27 | 6.47 |
| M05 | 3.75 | 5.21 | 5.53 | 6.43 | 6.22 |
| BH&H | 4.28 | 5.50 | 5.98 | 7.53 | 6.58 |
| BH&HLYP | 4.39 | 5.46 | 6.03 | 7.66 | 6.47 |
| BMK | 4.06 | 5.52 | 5.76 | 7.02 | 6.69 |
| M05-2X | 4.00 | 5.48 | 5.69 | 7.23 | 6.65 |
| HSE1PBE | 3.97 | 5.37 | 5.65 | 6.57 | 6.51 |
| CAM-B3LYP | 4.17 | 5.35 | 5.83 | 6.90 | 6.53 |
| LC-BLYP | 4.38 | 5.36 | 6.05 | 7.48 | 6.60 |
| LC-$\omega$PBE | 4.28 | 5.35 | 5.99 | 7.18 | 6.65 |
| EOM-CCSD | 4.38 | 5.11 | 6.02 | 7.12 | 7.05 |
| Exp. | 3.83[a] | 4.81 | 5.46[a] | 6.10 | 6.51 |

[a] 0-0 transition energy

Table 20: Calculated and experimental transition energies (eV) for pyrimidine. The reference for the experimental data are reported in the text. The SCF of BB95 and B1B95 did not converge.

| | $B_1$ $n \rightarrow \pi^*$ | $A_2$ $n \rightarrow \pi^*$ | $B_2$ $\pi \rightarrow \pi^*$ | $A_2$ $n \rightarrow \pi^*$ | $B_1$ $n \rightarrow \pi^*$ | $A_1$ $\pi \rightarrow \pi^*$ |
|---|---|---|---|---|---|---|
| RPA | 5.71 | 6.41 | 6.19 | 7.33 | 8.19 | 6.48 |
| CIS | 5.86 | 6.54 | 6.43 | 7.48 | 8.25 | 6.83 |
| CIS(D) | 4.63 | 5.05 | 5.53 | 6.07 | 6.37 | 7.14 |
| LSDA | 3.68 | 3.89 | 5.58 | 4.94 | 5.16 | 6.48 |
| BLYP | 3.80 | 4.03 | 5.52 | 5.10 | 5.33 | 6.32 |
| OLYP | 3.83 | 4.07 | 5.56 | 5.19 | 5.43 | 6.32 |
| BP86 | 3.79 | 4.02 | 5.56 | 5.11 | 5.34 | 6.41 |
| BVP86 | 3.79 | 4.02 | 5.56 | 5.11 | 5.34 | 6.41 |
| PBEPBE | 3.77 | 3.99 | 5.57 | 5.09 | 5.31 | 6.41 |
| HCTH | 3.84 | 4.08 | 5.57 | 5.18 | 5.43 | 6.41 |
| THCTH | 3.89 | 4.14 | 5.55 | 5.23 | 5.49 | 6.33 |
| BB95 | | | | | | |
| VSXC | 4.04 | 4.30 | 5.73 | 5.41 | 5.67 | 6.52 |
| TPSSTPSS | 3.98 | 4.24 | 5.64 | 5.36 | 5.61 | 6.47 |
| O3LYP | 4.09 | 4.39 | 5.67 | 5.50 | 5.77 | 6.49 |
| B3LYP | 4.26 | 4.59 | 5.71 | 5.65 | 5.95 | 6.50 |
| B3P86 | 4.25 | 4.59 | 5.75 | 5.67 | 5.96 | 6.57 |
| B3VP86 | 4.25 | 4.58 | 5.75 | 5.66 | 5.95 | 6.56 |
| PBE1PBE | 4.33 | 4.69 | 5.79 | 5.77 | 6.09 | 6.62 |
| B1B95 | | | | | | |
| THCTHHYB | 4.17 | 4.48 | 5.70 | 5.56 | 5.85 | 6.51 |
| TPSSh | 4.19 | 4.50 | 5.73 | 5.61 | 5.90 | 6.57 |
| M05 | 4.11 | 4.43 | 5.68 | 5.58 | 5.88 | 6.35 |
| BH&H | 4.76 | 5.26 | 5.98 | 6.23 | 6.70 | 6.71 |
| BH&HLYP | 4.86 | 5.37 | 5.94 | 6.35 | 6.84 | 6.60 |
| BMK | 4.47 | 4.90 | 5.94 | 5.95 | 6.33 | 6.80 |
| M05-2X | 4.48 | 4.98 | 5.96 | 5.98 | 6.40 | 6.77 |
| HSE1PBE | 4.31 | 4.68 | 5.79 | 5.74 | 6.06 | 6.60 |
| CAM-B3LYP | 4.54 | 4.91 | 5.78 | 5.98 | 6.29 | 6.64 |
| LC-BLYP | 4.83 | 5.25 | 5.85 | 6.28 | 6.62 | 6.76 |
| LC-$\omega$PBE | 4.68 | 5.05 | 5.81 | 6.17 | 6.45 | 6.80 |
| EOM-CCSD | 4.67 | 5.08 | 5.48 | 6.21 | 6.55 | 7.04 |
| Exp. | 3.85[a] | 4.62 | 5.12 | 5.52[a] | 5.90[a] | 6.70 |

[a] 0-0 transition energy

Table 21: Calculated and experimental transition energies (eV) for pyridazine. The reference for the experimental data are reported in the text. The SCF of BB95 and B1B95 did not converge.

| | $B_1$ $n \rightarrow \pi^*$ | $A_1$ $\pi \rightarrow \pi^*$ | $A_2$ $n \rightarrow \pi^*$ | $B_1$ $n \rightarrow \pi^*$ | $B_2$ $\pi \rightarrow \pi^*$ |
|---|---|---|---|---|---|
| RPA | 4.68 | 5.99 | 7.12 | 7.91 | 6.11 |
| CIS | 4.88 | 6.26 | 7.28 | 7.92 | 6.50 |
| CIS(D) | 4.20 | 5.43 | 5.59 | 7.83 | 7.16 |
| LSDA | 2.96 | 5.46 | 4.93 | 5.32 | 6.36 |
| BLYP | 3.14 | 5.39 | 5.03 | 5.45 | 6.21 |
| OLYP | 3.20 | 5.43 | 5.08 | 5.51 | 6.26 |
| BP86 | 3.13 | 5.44 | 5.03 | 5.45 | 6.25 |
| BVP86 | 3.13 | 5.44 | 5.04 | 5.45 | 6.25 |
| PBEPBE | 3.11 | 5.44 | 5.02 | 5.43 | 6.30 |
| HCTH | 3.20 | 5.43 | 5.09 | 5.52 | 6.23 |
| THCTH | 3.25 | 5.42 | 5.12 | 5.58 | 6.18 |
| BB95 | | | | | |
| VSXC | 3.40 | 5.60 | 5.28 | 5.77 | 6.39 |
| TPSSTPSS | 3.34 | 5.51 | 5.23 | 5.70 | 6.30 |
| O3LYP | 3.44 | 5.54 | 5.33 | 5.88 | 6.35 |
| B3LYP | 3.56 | 5.58 | 5.46 | 6.09 | 6.29 |
| B3P86 | 3.56 | 5.62 | 5.47 | 6.10 | 6.84 |
| B3VP86 | 3.55 | 5.61 | 5.46 | 6.09 | 6.40 |
| PBE1PBE | 3.63 | 5.66 | 5.56 | 6.22 | 6.45 |
| B1B95 | | | | | |
| THCTHHYB | 3.49 | 5.57 | 5.39 | 5.98 | 6.40 |
| TPSSh | 3.53 | 5.59 | 5.43 | 5.99 | 6.41 |
| M05 | 3.36 | 5.55 | 5.32 | 6.00 | 6.18 |
| BH&H | 3.96 | 5.84 | 5.99 | 6.86 | 6.53 |
| BH&HLYP | 4.08 | 5.79 | 6.07 | 6.99 | 6.41 |
| BMK | 3.70 | 5.80 | 5.71 | 6.48 | 6.65 |
| M05-2X | 3.66 | 5.83 | 5.75 | 6.57 | 6.65 |
| HSE1PBE | 3.61 | 5.65 | 5.54 | 6.20 | 6.44 |
| CAM-B3LYP | 3.81 | 5.65 | 5.76 | 6.46 | 6.50 |
| LC-BLYP | 4.01 | 5.72 | 6.10 | 6.85 | 6.58 |
| LC-$\omega$PBE | 3.92 | 5.69 | 5.96 | 6.65 | 6.63 |
| EOM-CCSD | 4.06 | 5.34 | 6.01 | 6.67 | 6.92 |
| Exp. | 3.60 | 5.00 | 5.30 | 6.00 | 6.50 |

Table 22: Calculated and experimental transition energies (eV) for S-tetrazine. All the transitions are $n \rightarrow \pi^*$. The reference for the experimental data are reported in the text. The SCF of BB95 and B1B95 did not converge.

| | $B_{3u}$ | $A_u$ | $A_u$ | $B_{3u}$ |
|---|---|---|---|---|
| RPA | 3.29 | 5.49 | 6.46 | 8.61 |
| CIS | 3.51 | 5.65 | 6.68 | 8.68 |
| CIS(D) | 2.76 | 4.13 | 5.52 | 6.80 |
| LSDA | 1.71 | 2.67 | 4.48 | 5.48 |
| BLYP | 1.88 | 2.85 | 4.64 | 5.65 |
| OLYP | 1.90 | 2.90 | 4.70 | 5.74 |
| BP86 | 1.85 | 2.84 | 4.63 | 5.65 |
| BVP86 | 1.85 | 2.84 | 4.63 | 5.66 |
| PBEPBE | 1.83 | 2.80 | 4.62 | 5.63 |
| HCTH | 1.89 | 2.91 | 4.69 | 5.74 |
| THCTH | 1.94 | 2.98 | 4.71 | 5.80 |
| BB95 | | | | |
| VSXC | 2.06 | 3.10 | 4.86 | 5.98 |
| TPSSTPSS | 2.02 | 3.07 | 4.83 | 5.92 |
| O3LYP | 2.10 | 3.25 | 4.95 | 6.10 |
| B3LYP | 2.24 | 3.48 | 5.08 | 6.30 |
| B3P86 | 2.22 | 3.47 | 5.08 | 6.31 |
| B3VP86 | 2.21 | 3.46 | 5.07 | 6.30 |
| PBE1PBE | 2.27 | 3.59 | 5.17 | 6.44 |
| B1B95 | | | | |
| THCTHHYB | 2.16 | 3.35 | 5.00 | 6.19 |
| TPSSh | 2.19 | 3.36 | 5.04 | 6.22 |
| M05 | 1.86 | 3.22 | 4.84 | 6.19 |
| BH&H | 2.59 | 4.22 | 5.56 | 7.07 |
| BH&HLYP | 2.71 | 4.36 | 5.65 | 7.22 |
| BMK | 2.34 | 3.82 | 5.31 | 6.68 |
| M05-2X | 2.26 | 3.93 | 5.33 | 6.78 |
| HSE1PBE | 2.26 | 3.57 | 5.15 | 6.42 |
| CAM-B3LYP | 2.46 | 3.84 | 5.36 | 6.67 |
| LC-BLYP | 2.63 | 4.24 | 5.64 | 7.03 |
| LC-$\omega$PBE | 2.52 | 4.01 | 5.53 | 6.84 |
| EOM-CCSD | 2.69 | 4.02 | 5.72 | 6.98 |
| Exp. | 2.25 | 3.40 | 5.00 | 6.34 |

Table 23: Mean absolute error (Mean AE), error root mean square (RMS), standard deviation ($\sigma$) and maximum absolute error (Max AE) for the first excited state and for all the states of all molecules (eV). BB95 and B1B95 are not reported as the SCF did not converge in six cases out of eleven.

| | All molecules | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $1^{st}$ state | | | | All states | | | |
| | Mean AE | RMS | $\sigma$ | Max AE | Mean AE | RMS | $\sigma$ | Max AE |
| RPA | 0.75 | 0.93 | 0.59 | 1.86 | 1.01 | 1.26 | 0.90 | 3.63 |
| CIS | 0.90 | 1.08 | 0.62 | 2.01 | 1.07 | 1.34 | 0.89 | 3.67 |
| CIS(D) | 0.35 | 0.45 | 0.30 | 0.78 | 0.49 | 0.61 | 0.61 | 1.83 |
| LSDA | 0.38 | 0.40 | 0.15 | 0.64 | 0.88 | 1.05 | 0.65 | 2.37 |
| BLYP | 0.41 | 0.52 | 0.33 | 1.03 | 1.23 | 1.49 | 0.91 | 2.96 |
| OLYP | 0.43 | 0.59 | 0.43 | 1.27 | 1.27 | 1.55 | 0.95 | 3.00 |
| BP86 | 0.34 | 0.39 | 0.20 | 0.68 | 1.08 | 1.32 | 0.83 | 2.77 |
| BVP86 | 0.34 | 0.39 | 0.21 | 0.69 | 1.08 | 1.32 | 0.83 | 2.78 |
| PBEPBE | 0.38 | 0.45 | 0.24 | 0.84 | 1.13 | 1.38 | 0.85 | 2.87 |
| HCTH | 0.31 | 0.39 | 0.24 | 0.80 | 1.00 | 1.22 | 0.77 | 2.62 |
| THCTH | 0.29 | 0.39 | 0.27 | 0.79 | 1.00 | 1.23 | 0.78 | 2.61 |
| VSXC | 0.22 | 0.29 | 0.27 | 0.62 | 0.97 | 1.24 | 0.87 | 2.60 |
| TPSSTPSS | 0.24 | 0.35 | 0.29 | 0.71 | 1.03 | 1.31 | 0.88 | 2.73 |
| O3LYP | 0.29 | 0.42 | 0.37 | 0.91 | 0.92 | 1.15 | 0.79 | 2.34 |
| B3LYP | 0.22 | 0.29 | 0.29 | 0.55 | 0.67 | 0.84 | 0.63 | 1.82 |
| B3P86 | 0.12 | 0.17 | 0.18 | 0.40 | 0.38 | 0.50 | 0.44 | 1.31 |
| B3VP86 | 0.17 | 0.21 | 0.21 | 0.40 | 0.57 | 0.74 | 0.58 | 1.73 |
| PBE1PBE | 0.18 | 0.23 | 0.24 | 0.48 | 0.55 | 0.69 | 0.58 | 1.62 |
| THCTHHYB | 0.18 | 0.23 | 0.22 | 0.38 | 0.67 | 0.87 | 0.65 | 1.99 |
| TPSSh | 0.20 | 0.27 | 0.27 | 0.51 | 0.80 | 1.03 | 0.77 | 2.25 |
| M05 | 0.24 | 0.29 | 0.24 | 0.47 | 0.62 | 0.75 | 0.53 | 1.71 |
| BH&H | 0.29 | 0.39 | 0.34 | 0.91 | 0.40 | 0.50 | 0.49 | 1.43 |
| BH&HLYP | 0.36 | 0.47 | 0.38 | 1.01 | 0.44 | 0.54 | 0.53 | 1.56 |
| BMK | 0.19 | 0.25 | 0.24 | 0.62 | 0.36 | 0.46 | 0.46 | 1.04 |
| M05-2X | 0.28 | 0.33 | 0.33 | 0.63 | 0.36 | 0.44 | 0.37 | 1.13 |
| HSE1PBE | 0.17 | 0.22 | 0.23 | 0.46 | 0.56 | 0.72 | 0.60 | 1.69 |
| CAM-B3LYP | 0.23 | 0.30 | 0.29 | 0.69 | 0.33 | 0.40 | 0.40 | 0.90 |
| LC-BLYP | 0.38 | 0.48 | 0.35 | 0.98 | 0.45 | 0.53 | 0.29 | 1.38 |
| LC-$\omega$PBE | 0.35 | 0.43 | 0.32 | 0.83 | 0.36 | 0.42 | 0.26 | 1.08 |
| EOM-CCSD | 0.35 | 0.44 | 0.27 | 0.82 | 0.27 | 0.36 | 0.30 | 1.02 |

Table 24: Mean absolute error (Mean AE), error root mean square (RMS), standard deviation ($\sigma$) and maximum absolute error (Max AE) for the first excited state and for all the states of all molecules (eV). BB95 and B1B95 are not reported as the SCF did not converge in six cases out of eleven.

| | $1^{st}$ state | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Alkenes+Carbonyls | | | | Azabenzenes | | | |
| | Mean AE | RMS | $\sigma$ | Max AE | Mean AE | RMS | $\sigma$ | Max AE |
| RPA | 0.30 | 0.37 | 0.25 | 0.57 | 1.29 | 1.32 | 0.34 | 1.86 |
| CIS | 0.42 | 0.49 | 0.27 | 0.73 | 1.48 | 1.50 | 0.32 | 2.01 |
| CIS(D) | 0.10 | 0.15 | 0.12 | 0.34 | 0.65 | 0.65 | 0.10 | 0.78 |
| LSDA | 0.35 | 0.36 | 0.12 | 0.54 | 0.42 | 0.45 | 0.18 | 0.64 |
| BLYP | 0.53 | 0.64 | 0.40 | 1.03 | 0.27 | 0.30 | 0.16 | 0.46 |
| OLYP | 0.59 | 0.76 | 0.53 | 1.27 | 0.23 | 0.27 | 0.15 | 0.40 |
| BP86 | 0.39 | 0.45 | 0.24 | 0.68 | 0.28 | 0.32 | 0.16 | 0.47 |
| BVP86 | 0.39 | 0.45 | 0.24 | 0.69 | 0.28 | 0.32 | 0.16 | 0.47 |
| PBEPBE | 0.45 | 0.52 | 0.29 | 0.84 | 0.30 | 0.34 | 0.16 | 0.49 |
| HCTH | 0.38 | 0.47 | 0.30 | 0.80 | 0.23 | 0.27 | 0.16 | 0.40 |
| THCTH | 0.37 | 0.48 | 0.33 | 0.79 | 0.20 | 0.23 | 0.16 | 0.35 |
| VSXC | 0.29 | 0.37 | 0.33 | 0.62 | 0.13 | 0.15 | 0.16 | 0.20 |
| TPSSTPSS | 0.33 | 0.44 | 0.34 | 0.71 | 0.15 | 0.17 | 0.16 | 0.26 |
| O3LYP | 0.43 | 0.56 | 0.40 | 0.91 | 0.12 | 0.15 | 0.17 | 0.24 |
| B3LYP | 0.28 | 0.35 | 0.23 | 0.55 | 0.15 | 0.21 | 0.18 | 0.41 |
| B3P86 | 0.10 | 0.13 | 0.09 | 0.27 | 0.15 | 0.21 | 0.18 | 0.40 |
| B3VP86 | 0.18 | 0.21 | 0.12 | 0.30 | 0.16 | 0.21 | 0.19 | 0.40 |
| PBE1PBE | 0.17 | 0.20 | 0.12 | 0.31 | 0.19 | 0.25 | 0.19 | 0.48 |
| THCTHHYB | 0.22 | 0.27 | 0.17 | 0.38 | 0.14 | 0.17 | 0.18 | 0.32 |
| TPSSh | 0.24 | 0.32 | 0.27 | 0.51 | 0.14 | 0.18 | 0.17 | 0.34 |
| M05 | 0.27 | 0.32 | 0.19 | 0.47 | 0.21 | 0.24 | 0.26 | 0.39 |
| BH&H | 0.09 | 0.10 | 0.10 | 0.14 | 0.53 | 0.57 | 0.23 | 0.91 |
| BH&HLYP | 0.12 | 0.14 | 0.15 | 0.21 | 0.64 | 0.67 | 0.23 | 1.01 |
| BMK | 0.11 | 0.12 | 0.12 | 0.16 | 0.28 | 0.34 | 0.22 | 0.62 |
| M05-2X | 0.31 | 0.32 | 0.35 | 0.46 | 0.24 | 0.33 | 0.25 | 0.63 |
| HSE1PBE | 0.16 | 0.19 | 0.12 | 0.27 | 0.17 | 0.24 | 0.19 | 0.46 |
| CAM-B3LYP | 0.10 | 0.13 | 0.08 | 0.22 | 0.38 | 0.42 | 0.20 | 0.69 |
| LC-BLYP | 0.18 | 0.26 | 0.25 | 0.54 | 0.61 | 0.64 | 0.25 | 0.98 |
| LC-$\omega$PBE | 0.22 | 0.32 | 0.31 | 0.65 | 0.50 | 0.54 | 0.23 | 0.83 |
| EOM-CCSD | 0.16 | 0.23 | 0.18 | 0.48 | 0.58 | 0.60 | 0.15 | 0.82 |

Table 25: Mean absolute error (Mean AE), error root mean square (RMS), standard deviation ($\sigma$) and maximum absolute error (Max AE) for the first excited state and for all the states of all molecules (eV). BB95 and B1B95 are not reported as the SCF did not converge in six cases out of eleven.

| | All states | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Alkenes+Carbonyls | | | | Azabenzenes | | | |
| | Mean AE | RMS | $\sigma$ | Max AE | Mean AE | RMS | $\sigma$ | Max AE |
| RPA | 0.81 | 1.04 | 0.80 | 1.89 | 1.39 | 1.59 | 0.95 | 3.63 |
| CIS | 0.85 | 1.09 | 0.80 | 1.94 | 1.49 | 1.71 | 0.86 | 3.67 |
| CIS(D) | 0.45 | 0.58 | 0.47 | 1.32 | 0.57 | 0.65 | 0.33 | 1.83 |
| LSDA | 1.08 | 1.23 | 0.60 | 2.37 | 0.50 | 0.55 | 0.43 | 1.12 |
| BLYP | 1.68 | 1.82 | 0.72 | 2.96 | 0.41 | 0.45 | 0.35 | 0.96 |
| OLYP | 1.76 | 1.90 | 0.72 | 3.00 | 0.37 | 0.41 | 0.34 | 0.90 |
| BP86 | 1.44 | 1.60 | 0.71 | 2.77 | 0.41 | 0.45 | 0.36 | 0.97 |
| BVP86 | 1.44 | 1.60 | 0.71 | 2.78 | 0.41 | 0.45 | 0.36 | 0.96 |
| PBEPBE | 1.51 | 1.67 | 0.71 | 2.87 | 0.42 | 0.46 | 0.37 | 0.99 |
| HCTH | 1.34 | 1.49 | 0.65 | 2.62 | 0.37 | 0.40 | 0.34 | 0.89 |
| THCTH | 1.36 | 1.50 | 0.65 | 2.61 | 0.34 | 0.37 | 0.31 | 0.82 |
| VSXC | 1.36 | 1.52 | 0.73 | 2.60 | 0.25 | 0.31 | 0.32 | 0.66 |
| TPSSTPSS | 1.44 | 1.60 | 0.71 | 2.73 | 0.27 | 0.32 | 0.31 | 0.72 |
| O3LYP | 1.30 | 1.42 | 0.56 | 2.34 | 0.20 | 0.26 | 0.27 | 0.55 |
| B3LYP | 0.91 | 1.02 | 0.46 | 1.82 | 0.20 | 0.27 | 0.25 | 0.59 |
| B3P86 | 0.47 | 0.59 | 0.35 | 1.31 | 0.21 | 0.29 | 0.25 | 0.63 |
| B3VP86 | 0.77 | 0.89 | 0.46 | 1.73 | 0.20 | 0.28 | 0.25 | 0.63 |
| PBE1PBE | 0.71 | 0.83 | 0.43 | 1.62 | 0.25 | 0.32 | 0.24 | 0.67 |
| THCTHHYB | 0.92 | 1.06 | 0.52 | 1.99 | 0.19 | 0.26 | 0.26 | 0.58 |
| TPSSh | 1.12 | 1.26 | 0.60 | 2.25 | 0.19 | 0.27 | 0.26 | 0.61 |
| M05 | 0.81 | 0.91 | 0.41 | 1.71 | 0.25 | 0.30 | 0.30 | 0.56 |
| BH&H | 0.30 | 0.38 | 0.36 | 0.92 | 0.59 | 0.67 | 0.34 | 1.43 |
| BH&HLYP | 0.33 | 0.39 | 0.38 | 0.92 | 0.66 | 0.75 | 0.40 | 1.56 |
| BMK | 0.35 | 0.46 | 0.35 | 1.04 | 0.39 | 0.46 | 0.25 | 0.92 |
| M05-2X | 0.34 | 0.40 | 0.37 | 0.80 | 0.41 | 0.50 | 0.29 | 1.13 |
| HSE1PBE | 0.73 | 0.86 | 0.46 | 1.69 | 0.24 | 0.31 | 0.25 | 0.67 |
| CAM-B3LYP | 0.32 | 0.39 | 0.23 | 0.90 | 0.37 | 0.43 | 0.24 | 0.80 |
| LC-BLYP | 0.37 | 0.44 | 0.25 | 1.06 | 0.59 | 0.67 | 0.31 | 1.38 |
| LC-$\omega$PBE | 0.28 | 0.34 | 0.23 | 0.77 | 0.49 | 0.55 | 0.25 | 1.08 |
| EOM-CCSD | 0.12 | 0.17 | 0.17 | 0.48 | 0.53 | 0.57 | 0.19 | 1.02 |