INTRAMOLECULAR BASIS SET SUPERPOSITION ERROR EFFECTS ON THE
PLANARITY OF BENZENE AND OTHER AROMATIC MOLECULES: A SOLUTION
TO THE PROBLEM.

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SUPPLEMENTARY INFORMATION
Software:

CP-opt driver

The CP-opt program automatically calls a slightly modified version (for higher accuracy of print out reasons) Gaussian98 in order to perform either energy, gradient optimizations or frequency corrected for Basis Set Superposition Error using counterpoise-type methods. Moreover, the user can define which fragment calculations are necessary in each case in terms of the fragment symmetry of the supermolecule and build any counterpoise-type function. The package includes several UNIX scripts (drive files) and FORTRAN 77 programs. From a conventional GAUSSIAN input file, 2N+1 input files for each calculation are generated and computed sequentially. Then CP-corrected, energy, gradient or hessian, depending on the calculation requested, is determined by the corresponding linear combination, either automatically or as defined by the user. In case of geometry optimisations, the new point in the CP-corrected PES is calculated externally using a generalized DIIS combined with variable metric optimizer and the next set of 2N+1 calculations are carried out again until the desired convergence.

One of us (P. S.) implemented automatic counterpoise correction to energy, gradients, second and third derivatives for up to 10 fragments into Gaussian, being readily available since versions Gaussian 98 rev A11. However, no handling of the fragment’s symmetry was implemented and generally NOSYMM keyword is necessary.

References to program packages used in this study:

Gaussian 98, Revision A.7:
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

Gaussian 03 Revision B.02:
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople; Gaussian, Inc., Wallingford CT, 2004.
Table S1. Uncorrected and Counterpoise-corrected optimized geometries of benzene ($D_{6h}$) at the Hartree-Fock level of theory and several basis sets. All data in the table were computed with Gaussian 03.

| Uncorrected | CP-corrected |
|-------------|--------------|
| **Basis set: 6-31+G** | |
| C          | 0.000000   | 1.389201 | 0.000000 | C | 0.000000 | 1.39236 | 0.000000 |
| C          | 1.202217   | 0.694100 | 0.000000 | C | 1.203113 | 0.694618 | 0.000000 |
| C          | 1.202217   | -0.694100 | 0.000000 | C | 1.203113 | -0.694618 | 0.000000 |
| C          | 0.000000   | -1.388201 | 0.000000 | C | 0.000000 | -1.389236 | 0.000000 |
| C          | -1.202217  | -0.694100 | 0.000000 | C | -1.203113 | -0.694618 | 0.000000 |
| C          | -1.202217  | 0.694100 | 0.000000 | C | -1.203113 | 0.694618 | 0.000000 |
| H          | 2.133621   | 1.231846 | 0.000000 | H | 2.133481 | 1.231766 | 0.000000 |
| H          | 2.133621   | -1.231846 | 0.000000 | H | 2.133481 | -1.231766 | 0.000000 |
| H          | 0.000000   | -2.463693 | 0.000000 | H | 0.000000 | -2.463532 | 0.000000 |
| H          | -2.133621  | -1.231846 | 0.000000 | H | -2.133481 | -1.231766 | 0.000000 |
| H          | -2.133621  | 1.231846 | 0.000000 | H | -2.133481 | 1.231766 | 0.000000 |
| H          | 0.000000   | 2.463693 | 0.000000 | H | 0.000000 | 2.463532 | 0.000000 |
| **Basis set: 6-311G** | |
| C          | 0.000000   | 1.387908 | 0.000000 | C | 0.000000 | 1.390868 | 0.000000 |
| C          | 1.201964   | 0.693954 | 0.000000 | C | 1.204527 | 0.695434 | 0.000000 |
| C          | 1.201964   | -0.693954 | 0.000000 | C | 1.204527 | -0.695434 | 0.000000 |
| C          | 0.000000   | -1.387908 | 0.000000 | C | 0.000000 | -1.390868 | 0.000000 |
| C          | -1.201964  | -0.693954 | 0.000000 | C | -1.204527 | -0.695434 | 0.000000 |
| C          | -1.201964  | 0.693954 | 0.000000 | C | -1.204527 | 0.695434 | 0.000000 |
| H          | 2.129169   | 1.229276 | 0.000000 | H | 2.133143 | 1.231571 | 0.000000 |
| H          | 2.129169   | -1.229276 | 0.000000 | H | 2.133143 | -1.231571 | 0.000000 |
| H          | 0.000000   | -2.458552 | 0.000000 | H | 0.000000 | -2.463141 | 0.000000 |
| H          | -2.129169  | -1.229276 | 0.000000 | H | -2.133143 | -1.231571 | 0.000000 |
| H          | -2.129169  | 1.229276 | 0.000000 | H | -2.133143 | 1.231571 | 0.000000 |
| H          | 0.000000   | 2.458552 | 0.000000 | H | 0.000000 | 2.463141 | 0.000000 |
| **Basis set: 6-311++G** | |
| C          | 0.000000   | 1.388674 | 0.000000 | C | 0.000000 | 1.391103 | 0.000000 |
| C          | 1.202627   | 0.694337 | 0.000000 | C | 1.204730 | 0.695551 | 0.000000 |
| C          | 1.202627   | -0.694337 | 0.000000 | C | 1.204730 | -0.695551 | 0.000000 |
| C          | 0.000000   | -1.388674 | 0.000000 | C | 0.000000 | -1.391103 | 0.000000 |
| C          | -1.202627  | -0.694337 | 0.000000 | C | -1.204730 | -0.695551 | 0.000000 |
| C          | -1.202627  | 0.694337 | 0.000000 | C | -1.204730 | 0.695551 | 0.000000 |
| H          | 2.130302   | 1.229331 | 0.000000 | H | 2.131206 | 1.230452 | 0.000000 |
| H          | 2.130302   | -1.229331 | 0.000000 | H | 2.131206 | -1.230452 | 0.000000 |
| H          | 0.000000   | -2.459861 | 0.000000 | H | 0.000000 | -2.460905 | 0.000000 |
| H          | -2.130302  | -1.229331 | 0.000000 | H | -2.131206 | -1.230452 | 0.000000 |
| H          | -2.130302  | 1.229331 | 0.000000 | H | -2.131206 | 1.230452 | 0.000000 |
Table S2. Uncorrected and Counterpoise-corrected optimized geometries of benzene \((D_6h)\) at the B3LYP level of theory and several basis sets. All data in the table were computed with Gaussian03.

| Basis set: | Uncorrected | CP-corrected |
|-----------|-------------|--------------|
| **6-31+G*** | | |
| C         | 0.000000   | 1.398539     | C 1.399810 | 0.000000 | 0.000000 |
| C         | 1.211171   | 0.699270     | C 0.699905 | 1.212271 | 0.000000 |
| C         | -0.699270  | 0.000000     | C -0.699905 | 1.212271 | 0.000000 |
| C         | 0.000000   | -1.398539    | C -1.399810 | 0.000000 | 0.000000 |
| C         | -1.211171  | -0.699270    | C -0.699905 | -1.212271 | 0.000000 |
| C         | -1.211171  | 0.699270     | C 0.699905 | -1.212271 | 0.000000 |
| H         | 2.152803   | 1.242922     | H 2.487691 | 0.000000 | 0.000000 |
| H         | 2.152803   | -1.242922    | H 1.243846 | 2.154404 | 0.000000 |
| H         | 0.000000   | -2.485843    | H -1.243846 | 2.154404 | 0.000000 |
| H         | -2.152803  | -1.242922    | H -2.487691 | 0.000000 | 0.000000 |
| H         | -2.152803  | 1.242922     | H -1.243846 | -2.154404 | 0.000000 |
| H         | 0.000000   | 2.485843     | H 1.243846 | -2.154404 | 0.000000 |
| **6-311G** | | |
| C         | 0.000000   | 1.398212     | C 1.400325 | 0.000000 | 0.000000 |
| C         | 1.210887   | 0.699106     | C 0.700162 | 1.212717 | 0.000000 |
| C         | -0.699106  | 0.000000     | C -0.700162 | 1.212717 | 0.000000 |
| C         | 0.000000   | -1.398212    | C -1.400325 | 0.000000 | 0.000000 |
| C         | -1.210887  | -0.699106    | C -0.700162 | -1.212717 | 0.000000 |
| C         | -1.210887  | 0.699106     | C 0.700162 | -1.212717 | 0.000000 |
| H         | 2.148028   | 1.240164     | H 2.485687 | 0.000000 | 0.000000 |
| H         | 2.148028   | -1.240164    | H 1.242843 | 2.152668 | 0.000000 |
| H         | 0.000000   | -2.480329    | H -1.242843 | 2.152668 | 0.000000 |
| H         | -2.148028  | -1.240164    | H -2.485687 | 0.000000 | 0.000000 |
| H         | -2.148028  | 1.240164     | H -1.242843 | -2.152668 | 0.000000 |
| H         | 0.000000   | 2.480329     | H 1.242843 | -2.152668 | 0.000000 |
| **6-311++G** | | |
| C         | 0.000000   | 1.398932     | C 1.400683 | 0.000000 | 0.000000 |
| C         | 1.211511   | 0.699466     | C 0.700341 | 1.213027 | 0.000000 |
| C         | -0.699466  | 0.000000     | C -0.700341 | 1.213027 | 0.000000 |
| C         | 0.000000   | -1.398932    | C -1.400683 | 0.000000 | 0.000000 |
| C         | -1.211511  | -0.699466    | C -0.700341 | -1.213027 | 0.000000 |
| C         | -1.211511  | 0.699466     | C 0.700341 | -1.213027 | 0.000000 |
| H         | 2.148891   | 1.240663     | H 2.483916 | 0.000000 | 0.000000 |
| H         | 2.148891   | -1.240663    | H 1.241908 | 2.151047 | 0.000000 |
| H         | 0.000000   | -2.481325    | H -1.241908 | 2.151047 | 0.000000 |
| H         | -2.148891  | -1.240663    | H -2.483916 | 0.000000 | 0.000000 |
| H         | -2.148891  | 1.240663     | H -1.241908 | -2.151047 | 0.000000 |
| H         | 0.000000   | 2.481325     | H 1.241908 | -2.151047 | 0.000000 |
Table S3. Uncorrected and Counterpoise-corrected optimized geometries of benzene at the MP2 (frozen-core) level of theory and several basis sets. All data in the table were computed with Gaussian03.

|        | Uncorrected | CP-corrected |
|--------|-------------|--------------|
| Basis set: 6-31+G* |
| C      | 0.000000   | 1.399190     | 0.000000   | C | 0.000000   | 1.405895   | 0.000000   |
| C      | 1.211734   | 0.699595     | 0.000000   | C | 1.217532   | 0.702943   | 0.000000   |
| C      | -1.211734  | -0.699595    | 0.000000   | C | -1.217532  | -0.702943  | 0.000000   |
| C      | 0.000000   | -1.399190    | 0.000000   | C | 0.000000   | -1.405895  | 0.000000   |
| H      | 2.154073   | 1.243655     | 0.000000   | H | 2.158394   | 1.246149   | 0.000000   |
| H      | -2.154073  | -1.243655    | 0.000000   | H | -2.158394  | -1.246149  | 0.000000   |
| Basis set: 6-311G |
| C      | 0.000000   | 1.408187     | 0.000000   | C | 0.000000   | 1.421201   | 0.000000   |
| C      | 1.219526   | 0.704093     | 0.000000   | C | 1.230796   | 0.710601   | 0.000000   |
| C      | -1.219526  | -0.704093    | 0.000000   | C | -1.230796  | -0.710601  | 0.000000   |
| C      | 0.000000   | -1.408187    | 0.000000   | C | 0.000000   | -1.421201  | 0.000000   |
| H      | 2.160815   | 1.247547     | 0.000000   | H | 2.172904   | 1.254527   | 0.000000   |
| H      | -2.160815  | -1.247547    | 0.000000   | H | -2.172904  | -1.254527  | 0.000000   |
| Basis set: 6-311++G |
| C      | 0.000000   | 1.409358     | 0.000000   | C | 0.000000   | 1.420684   | 0.000000   |
| C      | 1.220540   | 0.704679     | 0.000000   | C | 1.230351   | 0.710347   | 0.000000   |
| C      | -1.220540  | -0.704679    | 0.000000   | C | -1.230349  | -0.710344  | 0.000000   |
| C      | 0.000000   | -1.409358    | 0.000000   | C | 0.000000   | -1.420692  | 0.000000   |
| H      | 2.162738   | 1.248657     | 0.000000   | H | 2.170599   | 1.253192   | 0.000000   |
| H      | -2.162738  | -1.248657    | 0.000000   | H | -2.170592  | -1.253197  | 0.000000   |
| Basis set: 6-311++G |
| C      | 0.000000   | 2.497315     | 0.000000   | H | 0.000000   | 2.506387   | 0.000000   |
Table S4. Uncorrected and Counterpoise-corrected optimized geometries of benzene ($D_{6h}$) at the CISD (frozen-core) level of theory and several basis sets. All data in the table were computed with Gaussian 03 and with the CP-opt driver and Gaussian 98.

| Uncorrected | CP-corrected |
|-------------|--------------|
| Basis set: 6-31+G* | |
| C 0.000000 1.390170 0.000000 | C 0.000000 1.396273 0.000000 |
| C 1.203922 0.695085 0.000000 | C 1.209207 0.698136 0.000000 |
| C 1.203922 -0.695085 0.000000 | C 1.209207 -0.698136 0.000000 |
| C 0.000000 -1.390170 0.000000 | C 0.000000 -1.396273 0.000000 |
| C -1.203922 -0.695085 0.000000 | C -1.209207 -0.698136 0.000000 |
| C -1.203922 0.695085 0.000000 | C -1.209207 0.698136 0.000000 |
| H 2.140015 1.235538 0.000000 | H 0.000000 2.475974 0.000000 |
| H 2.140015 -1.235538 0.000000 | H 2.144256 -1.237987 0.000000 |
| H 0.000000 -2.471077 0.000000 | H 0.000000 -2.475974 0.000000 |
| H -2.140015 -1.235538 0.000000 | H -2.144256 -1.237987 0.000000 |
| H -2.140015 1.235538 0.000000 | H -2.144256 1.237987 0.000000 |
| Basis set: 6-311G | |
| C 0.000000 1.397548 0.000000 | C 0.000000 1.410922 0.000000 |
| C 1.210312 0.698774 0.000000 | C 1.221894 0.705461 0.000000 |
| C 1.210312 -0.698774 0.000000 | C 1.221894 -0.705461 0.000000 |
| C 0.000000 -1.397548 0.000000 | C 0.000000 -1.410922 0.000000 |
| C -1.210312 -0.698774 0.000000 | C -1.221894 -0.705461 0.000000 |
| C -1.210312 0.698774 0.000000 | C -1.221894 0.705461 0.000000 |
| H 2.146080 1.239040 0.000000 | H 0.000000 2.492507 0.000000 |
| H 2.146080 -1.239040 0.000000 | H 2.144256 -1.237987 0.000000 |
| H 0.000000 -2.478080 0.000000 | H 0.000000 -2.492507 0.000000 |
| H -2.146080 -1.239040 0.000000 | H -2.144256 -1.237987 0.000000 |
| H -2.146080 1.239040 0.000000 | H -2.144256 1.237987 0.000000 |
| H 0.000000 2.478080 0.000000 | H 0.000000 2.478080 0.000000 |
| Basis set: 6-311++G | |
| C 0.000000 1.398342 0.000000 | C 0.000000 1.410047 0.000000 |
| C 1.210999 0.699171 0.000000 | C -1.221137 0.705023 0.000000 |
| C 1.210999 -0.699171 0.000000 | C -1.221137 -0.705023 0.000000 |
| C 0.000000 -1.398342 0.000000 | C 0.000000 -1.410047 0.000000 |
| C -1.210999 -0.699171 0.000000 | C 1.221137 -0.705023 0.000000 |
| C -1.210999 0.699171 0.000000 | C 1.221137 0.705023 0.000000 |
| H 2.147405 1.239805 0.000000 | H 0.000000 2.469684 0.000000 |
| H 2.147405 -1.239805 0.000000 | H -2.156130 1.244842 0.000000 |
| H 0.000000 -2.479610 0.000000 | H -2.156130 -1.244842 0.000000 |
| H -2.147405 -1.239805 0.000000 | H -2.156130 -2.469684 0.000000 |
| H -2.147405 1.239805 0.000000 | H 2.156130 -1.244842 0.000000 |
| H 0.000000 2.479610 0.000000 | H 2.156130 1.244842 0.000000 |
Table S5. Uncorrected and Counterpoise-corrected optimized geometries of naphtalene (D$_{2h}$) using the 6-31G basis set at the Hartree-Fock, B3LYP and MP2(frozen-core) levels of theory. All data in the table were computed with Gaussian 03 and with the CP-opt driver and Gaussian 98.

|          | Uncorrected | Hartree-Fock | CP-corrected |
|----------|-------------|--------------|--------------|
|                  | X           | Y           | Z          | X           | Y          | Z          |
| C        | 0.000000    | 1.242708    | 1.394089   | C        | 0.000000    | 1.246488   | -1.395625 |
| C        | 0.000000    | 2.419453    | 0.707861   | C        | 0.000000    | 2.426369   | -0.709638 |
| C        | 0.000000    | 1.242708    | -1.394089  | C        | 0.000000    | 1.246488   | 1.395625  |
| C        | 0.000000    | 0.000000    | -0.706396  | C        | 0.000000    | 0.000000   | 0.706215  |
| H        | 0.000000    | 1.239297    | 2.468031   | H        | 0.000000    | 1.239576   | -2.469718 |
| H        | 3.353703    | 1.235401    |           | H        | 0.000000    | 3.360597   | -1.239072 |
| B3LYP    |              |             |            |          |             |            |            |
|                  | X           | Y           | Z          | X           | Y          | Z          |
| C        | 0.000000    | 1.247555    | 1.406165   | C        | -0.017220   | -0.000001  | -0.000858 |
| C        | 2.439495    | 0.709951    |            | C        | -0.018096   | -0.000022  | 1.382228  |
| C        | 2.439495    | -0.709951   |            | C        | 1.211572    | 0.000001   | 2.099200  |
| C        | 1.247555    | 1.406165    |            | C        | 2.415154    | 0.000027   | 1.417433  |
| C        | 0.000000    | -0.718906   |            | C        | 2.450101    | 0.000022   | -0.00947  |
| H        | 0.000000    | 1.244499    | 2.492649   | H        | -0.956264   | 0.000003   | -0.556193 |
| H        | 3.383950    | 2.492649    |            | H        | -0.960470   | 0.000079   | 1.930471  |
| MP2      |              |             |            |          |             |            |            |
|                  | X           | Y           | Z          | X           | Y          | Z          |
| C        | 0.000000    | 1.256377    | 1.419077   | C        | 0.000000    | 1.266069   | -1.427266 |
| C        | 2.459294    | 0.716303    |            | C        | 0.000000    | 2.480244   | -0.722826 |
| C        | 2.459294    | -0.716303   |            | C        | 0.000000    | 2.480244   | 0.722826  |
| C        | 1.256377    | -1.419077   |            | C        | 0.000000    | 1.266069   | 1.427266  |
| C        | 0.000000    | -0.722744   |            | C        | 0.000000    | 0.000000   | 0.719434  |
| H        | 1.255500    | 2.512632    |            | H        | 0.000000    | 1.255610   | -2.520806 |
| H        | 3.408476    | 1.254684    |            | H        | 0.000000    | 3.429509   | -1.263465 |
| H        | 3.408476    | -1.254684   |            | H        | 0.000000    | 3.429509   | 1.263465  |
| H        | 1.255500    | 2.512632    |            | H        | 0.000000    | 1.255610   | 2.520806  |
| C        | -1.256377   | -1.419077   |            | C        | 0.000000    | -1.266069  | 1.427266  |
| C        | -1.256377   | 1.419077    |            | C        | 0.000000    | -1.266069  | -1.427266 |
| C        | -2.459294   | 0.716303    |            | C        | 0.000000    | -2.480244  | -0.722826 |
| C        | -2.459294   | -0.716303   |            | C        | 0.000000    | -2.480244  | 0.722826  |
### Table S5: (cont.)

|         | X      | Y      | Z      |         | X      | Y      | Z      |
|---------|--------|--------|--------|---------|--------|--------|--------|
| H       | 0.000000 | -1.255500 | 2.512632 | H       | 0.000000 | -1.255610 | -2.520806 |
| H       | 0.000000 | -1.255500 | -2.512632 | H       | 0.000000 | -1.255610 | 2.520806  |
| H       | 0.000000 | -3.408476 | 1.254684 | H       | 0.000000 | -3.429509 | -1.263465 |
| H       | 0.000000 | -3.408476 | -1.254684 | H       | 0.000000 | -3.429509 | 1.263465  |

### Table S6. Uncorrected and Counterpoise-corrected optimized geometries of cyclipentadienil anion ($D_{5h}$) at the MP2/ 6-311G level of theory. All data in the table were computed with the CP-opt driver and Gaussian 98.

|       | Uncorrected     | CP-corrected |
|-------|-----------------|--------------|
|       | X    | Y    | Z    | X    | Y    | Z    |
| C     | 0.000000 | 1.215696 | 0.000000 | C     | 0.000000 | 1.227571 | 0.000000 |
| C     | 1.156195 | 0.375671 | 0.000000 | C     | 1.167489 | 0.379340 | 0.000000 |
| C     | 0.714568 | -0.983518 | 0.000000 | C     | 0.721548 | -0.993126 | 0.000000 |
| C     | -0.714568 | -0.983518 | 0.000000 | C     | -0.721548 | -0.993126 | 0.000000 |
| C     | -1.156195 | 0.375671 | 0.000000 | C     | -1.167489 | 0.379340 | 0.000000 |
| H     | 1.355696 | -1.865956 | 0.000000 | H     | 1.364151 | -1.877592 | 0.000000 |
| H     | 2.193562 | 0.712732 | 0.000000 | H     | 2.207242 | 0.717176 | 0.000000 |
| H     | -2.193562 | 0.712732 | 0.000000 | H     | -2.207242 | 0.717176 | 0.000000 |
| H     | 0.000000 | 2.306448 | 0.000000 | H     | 0.000000 | 2.320832 | 0.000000 |
| H     | -1.355696 | -1.865956 | 0.000000 | H     | -1.364151 | -1.877592 | 0.000000 |
Table S7. Uncorrected and Counterpoise-corrected harmonic vibrational frequencies (cm\(^{-1}\)) for benzene (\(\text{D}_6\)) at the Hartree-Fock level of theory. The average difference between uncorrected and CP-corrected frequencies is 1.6% and 1.3% for Hartree-Fock and B3LYP, respectively. All data in the table were computed with Gaussian 03.

### Hartree-Fock

| 6-31+G(d) | Uncorr. % diff | 6-311G | Uncorr. % diff | 6-311++G | Uncorr. % diff |
|-----------|----------------|--------|----------------|----------|----------------|
| CP-corrected | | CP-corrected | | CP-corrected | |
| E2U  | 448 | 451 | 0.7 | E2U  | 459 | 463 | 0.9 | E2U  | 449 | 462 | 3.1 |
| E2G  | 663 | 663 | 0.0 | E2G  | 688 | 683 | 0.7 | E2G  | 680 | 682 | 1.3 |
| A2U  | 745 | 760 | 2.0 | A2U  | 747 | 771 | 3.2 | A2U  | 723 | 772 | 1.0 |
| B2G  | 765 | 775 | 1.3 | B2G  | 784 | 794 | 1.3 | B2G  | 788 | 803 | 9.9 |
| E1G  | 940 | 960 | 2.1 | E1G  | 949 | 978 | 3.1 | E1G  | 939 | 983 | 2.0 |
| A1G  | 1073 | 1076 | 0.3 | A1G  | 1067 | 1070 | 0.3 | A1G  | 1091 | 1140 | 5.2 |
| E2U  | 1073 | 1108 | 3.3 | E2U  | 1081 | 1126 | 4.2 | E2U  | 1064 | 1185 | 19.4 |
| B2G  | 1092 | 1141 | 4.5 | B2G  | 1097 | 1152 | 5.0 | B1U  | 1129 | 1067 | 0.2 |
| B1U  | 1101 | 1097 | 0.4 | E1U  | 1135 | 1134 | 0.1 | E2U  | 1130 | 1123 | 2.3 |
| E1U  | 1133 | 1137 | 0.4 | B1U  | 1147 | 1124 | 2.0 | B2U  | 1122 | 1132 | 0.3 |
| B2U  | 1195 | 1201 | 0.5 | B2U  | 1237 | 1242 | 0.4 | B2G  | 1230 | 1243 | 0.2 |
| E2G  | 1288 | 1291 | 0.2 | E2G  | 1312 | 1304 | 0.6 | B2U  | 1285 | 1302 | 1.3 |
| B2U  | 1349 | 1353 | 0.3 | B2U  | 1372 | 1362 | 0.7 | B2G  | 1337 | 1361 | 1.4 |
| A2G  | 1505 | 1506 | 0.1 | A2G  | 1551 | 1524 | 1.7 | A2G  | 1506 | 1521 | 2.2 |
| E1U  | 1642 | 1644 | 0.1 | E1U  | 1662 | 1644 | 1.1 | E1U  | 1627 | 1640 | 1.6 |
| E2G  | 1782 | 1786 | 0.2 | E2G  | 1775 | 1772 | 0.2 | E2G  | 1755 | 1766 | 0.3 |
| B1U  | 3365 | 3351 | 0.4 | E2U  | 3314 | 3323 | 0.3 | E2U  | 3341 | 3313 | 1.1 |
| E2G  | 3376 | 3362 | 0.4 | E2G  | 3324 | 3334 | 0.3 | E2G  | 3351 | 3326 | 1.0 |
| E1U  | 3393 | 3380 | 0.4 | E1U  | 3343 | 3355 | 0.4 | E1U  | 3396 | 3347 | 0.8 |
| A1G  | 3403 | 3391 | 0.4 | A1G  | 3358 | 3371 | 0.4 | A1G  | 3383 | 3361 | 0.7 |

### B3LYP

| 6-31+G(d) | Uncorr. % diff | 6-311G | Uncorr. % diff | 6-311++G | Uncorr. % diff |
|-----------|----------------|--------|----------------|----------|----------------|
| CP-corrected | | CP-corrected | | CP-corrected | |
| E2U  | 408 | 412 | 1.0 | E2U  | 419 | 421 | 0.5 | E2U  | 409 | 418 | 2.2 |
| E2G  | 619 | 621 | 0.3 | E2G  | 644 | 640 | 0.5 | E2G  | 642 | 639 | 0.5 |
| A2U  | 678 | 689 | 1.6 | A2U  | 683 | 704 | 3.1 | A2U  | 671 | 703 | 4.8 |
| E1G  | 851 | 863 | 1.4 | E1G  | 860 | 884 | 2.9 | B2G  | 687 | 740 | 7.7 |
| B2G  | 708 | 712 | 0.6 | B2G  | 727 | 736 | 1.2 | E1G  | 843 | 887 | 5.2 |
| E2U  | 964 | 981 | 1.8 | E2U  | 971 | 1006 | 3.7 | E2U  | 932 | 1006 | 7.9 |
| B2G  | 994 | 1014 | 2.0 | B2G  | 1001 | 1009 | 0.8 | B2G  | 940 | 1046 | 11.3 |
| A1G  | 1014 | 1014 | 0.0 | A1G  | 1006 | 1044 | 3.8 | A1G  | 1004 | 1006 | 0.2 |
| B1U  | 1022 | 1019 | 0.3 | B1U  | 1061 | 1048 | 1.2 | B1U  | 1058 | 1054 | 0.4 |
| E1U  | 1062 | 1064 | 0.2 | E1U  | 1064 | 1064 | 0.0 | E1U  | 1062 | 1062 | 0.0 |
| B2U  | 1177 | 1184 | 0.6 | B2U  | 1204 | 1207 | 0.2 | B2U  | 1208 | 1206 | 0.2 |
| E2G  | 1199 | 1205 | 0.5 | E2G  | 1219 | 1221 | 0.2 | E2G  | 1220 | 1219 | 0.1 |
| B2U  | 1354 | 1355 | 0.1 | B2U  | 1337 | 1338 | 0.1 | B2U  | 1337 | 1337 | 0.0 |
| A2G  | 1385 | 1386 | 0.1 | A2G  | 1432 | 1418 | 1.0 | A2G  | 1428 | 1415 | 0.9 |
| E1U  | 1520 | 1523 | 0.2 | E1U  | 1538 | 1530 | 0.5 | E1U  | 1534 | 1526 | 0.5 |
| E2G  | 1644 | 1646 | 0.1 | E2G  | 1636 | 1634 | 0.1 | E2G  | 1631 | 1630 | 0.1 |
| B1U  | 3179 | 3174 | 0.2 | B1U  | 3116 | 3155 | 1.3 | B1U  | 3148 | 3149 | 0.0 |
| E2G  | 3188 | 3183 | 0.2 | E2G  | 3134 | 3166 | 1.0 | E2G  | 3159 | 3161 | 0.1 |
| E1U  | 3203 | 3199 | 0.1 | E1U  | 3153 | 3185 | 1.0 | E1U  | 3177 | 3180 | 0.1 |
| A1G  | 3213 | 3209 | 0.1 | A1G  | 3168 | 3200 | 1.0 | A1G  | 3190 | 3194 | 0.1 |
| Table S8. Uncorrected and Counterpoise-corrected harmonic vibrational frequencies (cm⁻¹) for benzene (D₆h) at the MP2 and CISD levels of theory. The average difference between uncorrected and CP-corrected frequencies is 17.8% and 9.8% for MP2 and CISD, respectively. Excluding the problematic out-of-plane vibrational modes the differences are 4.4% and 4.2%, respectively. All data in the table were computed with Gaussian 03 and Gaussian98. |
| --- |
| **MP2** |
| 6-31+G(d) | CP-corrected | Uncorr. % diff | 6-311G | CP-corrected | Uncorr. % diff | 6-311++G | CP-corrected | Uncorr. % diff |
| E2U | 384 | 379 | 1.3 | E2U | 382 | 333 | 12.8 | E2U | 409 | 470 | 53.4 |
| B2G | 473 | 182 | 61.5 | B2G | 442 | 722i | 263.3 | E2G | 631 | 627 | 0.7 |
| E2G | 613 | 618 | 0.8 | E2G | 625 | 630 | 0.8 | A2U | 703 | 573 | 18.4 |
| A2U | 659 | 672 | 2.0 | A2U | 650 | 620 | 4.6 | B2G | 730 | 721 | 1.3 |
| E1G | 824 | 829 | 0.6 | E1G | 812 | 736 | 9.4 | E1G | 890 | 620 | 30.4 |
| E2U | 894 | 877 | 1.9 | E2U | 861 | 648 | 24.7 | A1G | 961 | 984 | 2.3 |
| B2G | 896 | 859 | 4.1 | B2G | 877 | 779 | 11.2 | A1G | 1015 | 468i | 146.1 |
| A1G | 1004 | 1020 | 1.6 | A1G | 966 | 988 | 2.3 | E1U | 1031 | 1050 | 1.9 |
| B1U | 1026 | 1018 | 0.8 | E1U | 1034 | 1055 | 2.0 | B2U | 1054 | 1208 | 14.6 |
| E1U | 1061 | 1077 | 1.5 | B1U | 1050 | 1029 | 2.0 | B2G | 1093 | 1852i | 269.4 |
| B2U | 1181 | 1206 | 2.1 | B2U | 1183 | 1210 | 2.3 | B1U | 1192 | 1021 | 14.3 |
| E2G | 1204 | 1225 | 1.7 | E2G | 1203 | 1225 | 1.8 | E2G | 1209 | 1223 | 1.1 |
| A2G | 1388 | 1389 | 0.1 | A2G | 1423 | 1410 | 0.9 | A2G | 1426 | 1402 | 1.7 |
| B2U | 1439 | 1464 | 1.7 | B2U | 1330 | 1362 | 2.4 | B2U | 1342 | 1364 | 1.6 |
| E1U | 1516 | 1530 | 1.4 | E2G | 1593 | 1615 | 1.4 | E2G | 1594 | 1609 | 0.9 |
| B2G | 1640 | 1660 | 1.2 | B2G | 1593 | 1615 | 1.4 | B2G | 1594 | 1609 | 0.9 |
| E2G | 3226 | 3208 | 0.6 | E2G | 3139 | 3145 | 2.0 | A1G | 3171 | 3150 | 0.6 |
| B1U | 3226 | 3208 | 0.6 | B2G | 3139 | 3145 | 2.0 | B1U | 3226 | 3183 | 1.7 |
| E1U | 3249 | 3232 | 0.5 | E2G | 3139 | 3145 | 2.0 | E1U | 3249 | 3183 | 1.7 |
| A1G | 3257 | 3242 | 0.5 | E2G | 3242 | 3249 | 0.5 | A1G | 3257 | 3242 | 0.5 |
| **CISD** |
| 6-31+G(d) | CP-corrected | Uncorr. % diff | 6-311G | CP-corrected | Uncorr. % diff | 6-311++G | CP-corrected | Uncorr. % diff |
| E2U | 426 | 418 | 1.9 | E2U | 382 | 339 | 3.9 | E2U | 455 | 281 | 38.2 |
| E2G | 639 | 643 | 0.6 | B2G | 442 | 189i | 142.8 | E2G | 653 | 650 | 0.5 |
| A2U | 713 | 720 | 1.0 | E2G | 625 | 652 | 4.3 | A2U | 761 | 652 | 14.3 |
| B2G | 716 | 591 | 17.5 | A2U | 650 | 678 | 4.3 | B2G | 875 | 801 | 8.5 |
| E1G | 904 | 899 | 0.6 | E2G | 812 | 830 | 2.2 | E2G | 991 | 666 | 32.8 |
| E2U | 1028 | 999 | 3.8 | B2G | 861 | 839 | 2.6 | B2U | 1060 | 1057 | 0.3 |
| A1G | 1047 | 1061 | 1.4 | B2G | 877 | 847 | 3.4 | A1G | 1011 | 1031 | 2.0 |
| B2G | 1049 | 977 | 7.1 | B2G | 877 | 847 | 3.4 | E1U | 1089 | 768 | 29.5 |
| B1U | 1063 | 1055 | 0.8 | E1U | 1034 | 1093 | 5.7 | B2U | 1176 | 1215 | 3.3 |
| E1U | 1099 | 1115 | 1.5 | E1U | 1034 | 1093 | 5.7 | E1U | 1216 | 1090 | 10.4 |
| B2U | 1190 | 1218 | 2.4 | B2U | 1183 | 1215 | 2.7 | E2G | 1250 | 1255 | 0.4 |
| E2G | 1241 | 1261 | 1.6 | E2G | 1203 | 1257 | 4.5 | B2G | 1320 | 1321 | 0.1 |
| B2G | 1335 | 1358 | 1.7 | B2G | 1330 | 1320 | 0.8 | A2G | 1465 | 1448 | 1.2 |
| A2G | 1446 | 1445 | 0.1 | A2G | 1423 | 1454 | 2.2 | E1U | 1583 | 1570 | 0.8 |
| E1U | 1582 | 1594 | 0.8 | E1U | 1515 | 1574 | 3.9 | B2G | 1591 | 1384i | 187.0 |
| E2G | 1724 | 1743 | 1.1 | E2G | 1593 | 1697 | 6.5 | E2G | 1678 | 1691 | 0.8 |
| B1U | 3302 | 3288 | 0.4 | B1U | 3129 | 3205 | 2.4 | B1U | 3206 | 3187 | 0.6 |
| E2G | 3311 | 3299 | 0.4 | E2G | 3139 | 3216 | 2.5 | E2G | 3224 | 3202 | 0.7 |
| E1U | 3327 | 3316 | 0.3 | E1U | 3156 | 3237 | 2.6 | E1U | 3252 | 3225 | 0.8 |
| A1G | 3337 | 3327 | 0.3 | A1G | 3170 | 3254 | 2.6 | A1G | 3270 | 3243 | 0.8 |
| HF  | CP-corrected | HF   | % diff | B3LYP CP-corrected | B3LYP % diff | MP2 CP-corrected | MP2 % diff |
|-----|--------------|------|--------|--------------------|--------------|-----------------|------------|
| B3U | 188          | 193  | 2.9    | 176                | 180          | 159             | 159        |
| AU  | 209          | 209  | 0.1    | 192                | 192          | 181             | 177        |
| B1U | 397          | 400  | 0.7    | 373                | 373          | 363             | 369        |
| B1G | 436          | 441  | 1.0    | 401                | 403          | 368             | 359        |
| B2G | 533          | 538  | 1.0    | 490                | 490          | 464             | 419        |
| B3U | 542          | 551  | 1.5    | 495                | 500          | 450             | 426        |
| AG  | 564          | 566  | 0.2    | 531                | 531          | 516             | 523        |
| B3G | 572          | 573  | 0.1    | 530                | 531          | 522             | 523        |
| B2U | 700          | 700  | 0.0    | 647                | 649          | 655             | 450        |
| AU  | 701          | 709  | 1.1    | 654                | 654          | 570             | -402       |
| B1G | 795          | 831  | 4.5    | 734                | 748          | 638             | 642        |
| AG  | 837          | 839  | 0.2    | 782                | 782          | 691             | 680        |
| B3U | 873          | 915  | 4.8    | 793                | 800          | 744             | 716        |
| B2G | 879          | 891  | 1.4    | 806                | 821          | 764             | 769        |
| B1U | 888          | 885  | 0.4    | 828                | 826          | 804             | 776        |
| AU  | 927          | 976  | 5.2    | 852                | 873          | 814             | 819        |
| B2G | 970          | 1039 | 7.2    | 892                | 922          | 816             | 783        |
| B1G | 1055         | 1122 | 6.4    | 977                | 973          | 883             | 838        |
| B3G | 1062         | 1054 | 0.7    | 950                | 977          | 886             | 839        |
| B3U | 1071         | 1148 | 7.1    | 966                | 997          | 897             | 821        |
| AU  | 1081         | 1172 | 8.4    | 990                | 1021         | 916             | 855        |
| B2G | 1086         | 1183 | 8.9    | 1002               | 1030         | 967             | 958        |
| B2U | 1091         | 1099 | 0.7    | 1046               | 1052         | 1011            | 1034       |
| AG  | 1122         | 1127 | 0.4    | 1058               | 1062         | 1028            | 1048       |
| B2U | 1236         | 1242 | 0.5    | 1172               | 1175         | 1154            | 1168       |
| B1U | 1266         | 1265 | 0.1    | 1194               | 1200         | 1172            | 1195       |
| B3G | 1290         | 1292 | 0.1    | 1206               | 1216         | 1187            | 1220       |
| AG  | 1313         | 1313 | 0.0    | 1211               | 1218         | 1197            | 1224       |
| B2U | 1330         | 1333 | 0.2    | 1255               | 1260         | 1227            | 1257       |
| B3G | 1409         | 1403 | 0.5    | 1306               | 1303         | 1285            | 1292       |
| B1U | 1414         | 1415 | 0.0    | 1316               | 1320         | 1295            | 1315       |
| B2U | 1501         | 1497 | 0.3    | 1421               | 1419         | 1409            | 1429       |
| AG  | 1513         | 1519 | 0.4    | 1430               | 1431         | 1415            | 1425       |
| B1U | 1582         | 1565 | 1.1    | 1464               | 1453         | 1447            | 1441       |
| B3G | 1645         | 1636 | 0.5    | 1525               | 1520         | 1495            | 1501       |
| AG  | 1652         | 1638 | 0.9    | 1527               | 1521         | 1502            | 1505       |
| B2U | 1694         | 1689 | 0.3    | 1574               | 1572         | 1537            | 1550       |
| AG  | 1781         | 1781 | 0.0    | 1632               | 1631         | 1593            | 1603       |
| B1U | 1806         | 1804 | 0.1    | 1661               | 1660         | 1608            | 1625       |
| B3G | 1845         | 1846 | 0.1    | 1690               | 1690         | 1644            | 1669       |
| B3G | 3349         | 3347 | 0.1    | 3154               | 3185         | 3164            | 3158       |
| B1U | 3351         | 3349 | 0.1    | 3156               | 3186         | 3167            | 3159       |
| B2U | 3353         | 3352 | 0.0    | 3158               | 3189         | 3167            | 3160       |
| AG  | 3358         | 3357 | 0.1    | 3161               | 3192         | 3170            | 3163       |
| B3G | 3368         | 3370 | 0.1    | 3172               | 3205         | 3184            | 3184       |
| B1U | 3370         | 3372 | 0.1    | 3174               | 3206         | 3184            | 3184       |
| B2U | 3380         | 3386 | 0.2    | 3186               | 3221         | 3196            | 3202       |
| AG  | 3382         | 3388 | 0.2    | 3188               | 3222         | 3198            | 3203       |
Table S10. Uncorrected and Counterpoise-corrected harmonic vibrational frequencies (cm\(^{-1}\)) for indenyl anion (C\(_{2v}\)) at the MP2/6-311G level of theory. All data in the table were computed with the CP-opt driver and Gaussian 98.

|              | MP2 CP-corrected | MP2       | % diff |
|--------------|------------------|-----------|--------|
| B1           | 197              | 199       | 1.0    |
| A2           | 221              | 305       | 38.2   |
| A2           | 331              | -1072     | 424.3  |
| B1           | 363              | 444       | 22.3   |
| B2           | 390              | 391       | 0.3    |
| A1           | 550              | 544       | 1.2    |
| B2           | 604              | 594       | 1.6    |
| A2           | 604              | -458      | 175.8  |
| B1           | 620              | 609       | 1.7    |
| B1           | 660              | 570       | 13.6   |
| A2           | 705              | 523       | 25.9   |
| A1           | 733              | 730       | 0.4    |
| B1           | 781              | 504       | 35.5   |
| B1           | 823              | -200      | 124.3  |
| A2           | 848              | -125      | 114.7  |
| A2           | 869              | 677       | 22.1   |
| A1           | 874              | 874       | 0.0    |
| B2           | 891              | 875       | 1.8    |
| A1           | 986              | 979       | 0.8    |
| A1           | 1034             | 1029      | 0.4    |
| B2           | 1046             | 1049      | 0.3    |
| B1           | 1058             | -555      | 152.4  |
| B2           | 1111             | 1104      | 0.6    |
| A1           | 1167             | 1169      | 0.1    |
| B2           | 1208             | 1195      | 1.1    |
| B2           | 1250             | 1228      | 1.7    |
| A1           | 1259             | 1242      | 1.3    |
| A1           | 1349             | 1337      | 0.9    |
| B2           | 1383             | 1350      | 2.4    |
| B2           | 1424             | 1405      | 1.3    |
| A1           | 1451             | 1422      | 2.0    |
| B2           | 1484             | 1463      | 1.4    |
| A1           | 1493             | 1468      | 1.7    |
| A1           | 1543             | 1518      | 1.6    |
| B2           | 1590             | 1561      | 1.9    |
| B2           | 3064             | 3061      | 0.1    |
| A1           | 3072             | 3069      | 0.1    |
| A1           | 3072             | 3076      | 0.1    |
| B2           | 3089             | 3088      | 0.0    |
| B2           | 3108             | 3110      | 0.1    |
| A1           | 3109             | 3110      | 0.0    |
| A1           | 3123             | 3124      | 0.0    |
Table S11. Uncorrected and Counterpoise-corrected harmonic vibrational frequencies (cm⁻¹) for cyclopentadienyl anion ($D_{5h}$) at the MP2/6-311G level of theory. All data in the table were computed with the CP-opt driver and Gaussian 98.

| Mode   | Uncorrected | MP2 CP-corrected | MP2 | % diff |
|--------|-------------|------------------|-----|--------|
| E2"    | 614         | -401             | 640 | 165.3  |
| E1"    | 640         | 284              | 680 | 55.7   |
| A2"    | 680         | 523              | 848 | 23.0   |
| E2"    | 848         | 632              | 854 | 25.4   |
| E2'    | 854         | 860              | 995 | 0.6    |
| E1'    | 995         | 1020             | 1065| 2.5    |
| E2'    | 1065        | 1089             | 1089| 2.3    |
| A1'    | 1089        | 1115             | 1311| 2.4    |
| A2'    | 1311        | 1298             | 1383| 1.0    |
| E2'    | 1383        | 1402             | 1449| 1.4    |
| E1'    | 1449        | 1454             | 3060| 0.4    |
| E2'    | 3060        | 3081             | 3087| 0.7    |
| E1'    | 3087        | 3111             | 3119| 0.8    |
| A1'    | 3119        | 3145             |     | 0.8    |