

# Supplementary Information for

The source of some empirical density functionals dispersion forces

A. V. Leonov<sup>a,b</sup>, D. U. Zaripov<sup>b,c</sup>, R. Yu. Dokin<sup>b</sup>, T. V. Losev<sup>a,b</sup>, I. S. Gerasimov<sup>b</sup>, M. G. Medvedev<sup>b,c</sup>

<sup>a</sup>*M. V. Lomonosov Moscow State University, Leninskiye Gory, 1, Moscow, 119991, Russia*

<sup>b</sup>*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,  
Leninsky prospect, 47, Moscow, 119991, Russia*

<sup>c</sup>*HSE University, Myasnitskaya ulitsa, 20, Moscow, 101000, Russia*

Correspondence to:  
medvedev.m.g@gmail.com

## **This PDF file includes:**

List of studied functionals, Energy calculations, Force calculations, Issues solving.

## **Other Supplementary Information for this manuscript includes the following:**

All code used for the analyses is publicly available on GitHub at  
[https://github.com/TheorChemGroup/Hellmann-Feynman\\_2024](https://github.com/TheorChemGroup/Hellmann-Feynman_2024)

## List of studied functionals

Physically-grounded and well-tested: SLATER<sup>1,2</sup>, AM05<sup>3,4</sup>, BLYP<sup>5-7</sup>, PBE<sup>8,9</sup>, PBESOL<sup>10</sup>, HCTH407<sup>11</sup>, TPSS<sup>12,13</sup>, revTPSS<sup>14</sup>, APF<sup>15</sup>, B1LYP<sup>16</sup>, B3LYPV1R<sup>17</sup>, B97<sup>18</sup>, BHHLYP<sup>19</sup>, CAMB3LYP<sup>20</sup>, PBE0<sup>21,22</sup>, TPSSH<sup>23</sup>, HSE06<sup>24-26</sup>, LRC-WPBEH<sup>27</sup>, WB97<sup>28</sup>, WB97X<sup>28</sup>.

Rare functionals: DLDF<sup>29</sup>, B97-1<sup>30</sup>, B97-2<sup>31</sup>, B97-3<sup>32</sup>, EDF1<sup>33</sup>, EDF2<sup>34</sup>, VSXC<sup>35</sup>, CHACHIYO<sup>36,37</sup>

QTP family: CAMQTP00<sup>38</sup>, CAMQTP01<sup>39</sup>, CAMQTP02<sup>40</sup>, LC-QTP<sup>40</sup>, QTP17<sup>41</sup>.  
SCAN family: SCAN<sup>42</sup>, RSCAN<sup>43</sup>, r<sup>2</sup>SCAN<sup>44</sup>.

Minnesota family: MPWLYP1W<sup>45</sup>, GAM<sup>46</sup>, M05<sup>47</sup>, M052X<sup>48</sup>, M06<sup>49</sup>, M062X<sup>49</sup>, M06HF<sup>50</sup>, M06L<sup>51</sup>, M08-HX<sup>52</sup>, M08-SO<sup>52</sup>, M11<sup>53</sup>, M11L<sup>54</sup>, MN12L<sup>55</sup>, MN12SX<sup>56</sup>, MN15<sup>57</sup>, MN15L<sup>58</sup>, N12<sup>59</sup>, N12SX<sup>56</sup>, SOGGA11X<sup>60</sup>, revM06<sup>61</sup>, revM06L<sup>62</sup>, revM11<sup>63</sup>, HLE16<sup>64</sup>, HLE17<sup>65</sup>.

Functionals fitted on exchange-correlation potentials: HCTH-P14<sup>66</sup>, HCTH-P76<sup>66</sup>.

## Energy calculations

Version of GAMESS-US and LIBXC: LIBXC ver 5.0.0 (DFT except R2SCAN, HCTH-P76) and 5.1.4 (R2SCAN, HCTH-P76, He, Ne => binding energies); GAMESS version is locally modified (post 2020.2)).

Energy binding is calculated with counterpoise correction, as

$$E_{\text{binding}} = E_{\text{AB@AB}} - E_{\text{A@AB}} - E_{\text{B@AB}},$$

where energies of single atoms  $E_{\text{A@AB}}$  and  $E_{\text{B@AB}}$ , and energy of molecule  $E_{\text{AB@AB}}$  was calculated in same basis set, which contains basis functions of both atoms A and B.

Convergence method is selected as DIIS. SOSCF tends to obtain more broken forces results.

## Force calculations

Hellmann-Feynman forces and differences of wavefunctions near the equilibrium state (for all molecules were taken interatomic distance as 3.0Å) were obtained via MultiWFN (ver. 3.8(dev), release: 2021-Jan-29). Forces of molecules are net difference of forces of atoms. Forces were calculated to be positive at the start of forces curve to the most functionals, because of the internal coordinates. Grid of wavefunction difference operation was taken as number of points for Becke numerical quadrature in radial/on spherical surface to be equal 300/1454, respectively.

Distance where forces vanish were calculated by approximating the segment as a straight line between two neighbor points and finding the point where force crosses zero level.

Obtaining QCF through approximating by a spline function (spline.fun() in R) is unsuccessful due to low-resolution energy curve, so QCF were obtained analytically (by “force” flag) in Gaussian and numerically (RUNTYP=gradient) in GAMESS-US.

### Issues solving

Pulay stress relationship to basis. Pulay *really* tends to low error with increasing of basis set. We selected the largest basis set in Dunning group in which HFF are obtainable.

Basis	QCF	HFF	Pulay	Pulay/QCF
ACCQ	-6.48E-05	2.84E-04	-3.49E-04	538.27%
ACC5	-6.20E-05	4.91E-05	-1.11E-04	179.19%
ACC6 (-2I)	-5.87E-05	-6.47E-05	6.00E-06	-10.22%

*Calculations were performed in CCSD-full with different basis in HeNe system at 3.5Å.*

Higher period noble gases dimers weren't calculated due to high computational cost in large basis set.

Distance of energy minimum was calculated via QCF to specify minimum gained by energy. Values of M11, MN12L, MN12SX, MN15L, SCAN were corrected because of forces were numerically unstable. And also, BHHLYP, EDF2 and SCAN, because they had local minimum of energy, but not global. Mid bond functions and counterpoise corrections were tested. Mid bond functions did not affect so much on accuracy of calculations, however counterpoise correction did, so computation was performed with CP correction.

Some points on energy and QCF curve are found to be numerically unstable, specifically Minnesota functionals: M06HF, M06L, a little bit M11, M11L, MN12L, MN12SX, MN15, MN15L and SCAN, SCAN0. The functional MN12L was excluded from further analysis because of instabilities in energy curve, while for MN12SX, an anomaly in the potential energy curve of the HeNe dimer at an internuclear distance of 5.6Å in counterpoise correction calculation was interpolated with nearest neighbors. We tried to converge them (as well as Minnesota functionals) in Gamess-US using different approaches. TASK, revSCAN, SOGGA11 failed to converge its energy in some points of the curve regardless of the method we used so they are not presented here.

Initial flags:

`$SCF DIRSCF=.TRUE. DIIS=.T. $END.`

Flags that may help:

`$SCF DIRSCF=.TRUE. VTSCAL=.FALSE. $END`

`$SCF NOCONV=.T. DEM=.T. EXTRAP=.T. RSTRCT=.T. $END`

`$SCF DEM=.T. EXTRAP=.T. RSTRCT=.T. $END`

`$SCF EXTRAP=.T. RSTRCT=.T. $END`

`$SCF DIIS=.T. EXTRAP=.T. RSTRCT=.T. $END`

`$SCF EXTRAP=.T. DAMP=.T. $END`

- (1) Dirac, P. A. M. Note on Exchange Phenomena in the Thomas Atom. *Math. Proc. Camb. Phil. Soc.* **1930**, 26 (3), 376–385. <https://doi.org/10.1017/S0305004100016108>.
- (2) Bloch, F. Bemerkung zur Elektronentheorie des Ferromagnetismus und der elektrischen Leitfähigkeit. *Z. Physik* **1929**, 57 (7–8), 545–555. <https://doi.org/10.1007/BF01340281>.
- (3) Armiento, R.; Mattsson, A. E. Functional Designed to Include Surface Effects in Self-Consistent Density Functional Theory. *Phys. Rev. B* **2005**, 72 (8), 085108. <https://doi.org/10.1103/PhysRevB.72.085108>.
- (4) Mattsson, A. E.; Armiento, R.; Paier, J.; Kresse, G.; Wills, J. M.; Mattsson, T. R. The AM05 Density Functional Applied to Solids. *The Journal of Chemical Physics* **2008**, 128 (8), 084714. <https://doi.org/10.1063/1.2835596>.
- (5) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, 38 (6), 3098–3100. <https://doi.org/10.1103/PhysRevA.38.3098>.
- (6) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chemical Physics Letters* **1989**, 157 (3), 200–206. [https://doi.org/10.1016/0009-2614\(89\)87234-3](https://doi.org/10.1016/0009-2614(89)87234-3).
- (7) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, 37 (2), 785–789. <https://doi.org/10.1103/PhysRevB.37.785>.
- (8) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, 78 (7), 1396–1396. <https://doi.org/10.1103/PhysRevLett.78.1396>.
- (9) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (10) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. *Phys. Rev. Lett.* **2008**, 100 (13), 136406. <https://doi.org/10.1103/PhysRevLett.100.136406>.
- (11) Boese, A. D.; Handy, N. C. A New Parametrization of Exchange–Correlation Generalized Gradient Approximation Functionals. *The Journal of Chemical Physics* **2001**, 114 (13), 5497–5503. <https://doi.org/10.1063/1.1347371>.
- (12) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, 91 (14), 146401. <https://doi.org/10.1103/PhysRevLett.91.146401>.
- (13) Perdew, J. P.; Tao, J.; Staroverov, V. N.; Scuseria, G. E. Meta-Generalized Gradient Approximation: Explanation of a Realistic Nonempirical Density Functional. *The Journal of Chemical Physics* **2004**, 120 (15), 6898–6911. <https://doi.org/10.1063/1.1665298>.
- (14) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. Workhorse Semilocal Density Functional for Condensed Matter Physics and Quantum Chemistry. *Phys. Rev. Lett.* **2009**, 103 (2), 026403. <https://doi.org/10.1103/PhysRevLett.103.026403>.
- (15) Austin, A.; Petersson, G. A.; Frisch, M. J.; Dobek, F. J.; Scalmani, G.; Throssell, K. A Density Functional with Spherical Atom Dispersion Terms. *J. Chem. Theory Comput.* **2012**, 8 (12), 4989–5007. <https://doi.org/10.1021/ct300778e>.
- (16) Adamo, C.; Barone, V. Toward Reliable Adiabatic Connection Models Free from Adjustable Parameters. *Chemical Physics Letters* **1997**, 274 (1–3), 242–250. [https://doi.org/10.1016/S0009-2614\(97\)00651-9](https://doi.org/10.1016/S0009-2614(97)00651-9).
- (17) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *The Journal of Physical Chemistry* **1994**, 98 (45), 11623–11627. <https://doi.org/10.1021/j100096a001>.

- (18) Becke, A. D. Density-Functional Thermochemistry. V. Systematic Optimization of Exchange-Correlation Functionals. *The Journal of Chemical Physics* **1997**, *107* (20), 8554–8560. <https://doi.org/10.1063/1.475007>.
- (19) Becke, A. D. A New Mixing of Hartree–Fock and Local Density-functional Theories. *The Journal of Chemical Physics* **1993**, *98* (2), 1372–1377. <https://doi.org/10.1063/1.464304>.
- (20) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chemical Physics Letters* **2004**, *393* (1–3), 51–57. <https://doi.org/10.1016/j.cplett.2004.06.011>.
- (21) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *The Journal of Chemical Physics* **1999**, *110* (13), 6158–6170. <https://doi.org/10.1063/1.478522>.
- (22) Ernzerhof, M.; Scuseria, G. E. Assessment of the Perdew–Burke–Ernzerhof Exchange–Correlation Functional. *The Journal of Chemical Physics* **1999**, *110* (11), 5029–5036. <https://doi.org/10.1063/1.478401>.
- (23) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. Comparative Assessment of a New Nonempirical Density Functional: Molecules and Hydrogen-Bonded Complexes. *The Journal of Chemical Physics* **2003**, *119* (23), 12129–12137. <https://doi.org/10.1063/1.1626543>.
- (24) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *The Journal of Chemical Physics* **2003**, *118* (18), 8207–8215. <https://doi.org/10.1063/1.1564060>.
- (25) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: “Hybrid Functionals Based on a Screened Coulomb Potential” [J. Chem. Phys. 118, 8207 (2003)]. *The Journal of Chemical Physics* **2006**, *124* (21), 219906. <https://doi.org/10.1063/1.2204597>.
- (26) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the Exchange Screening Parameter on the Performance of Screened Hybrid Functionals. *The Journal of Chemical Physics* **2006**, *125* (22), 224106. <https://doi.org/10.1063/1.2404663>.
- (27) Rohrdanz, M. A.; Martins, K. M.; Herbert, J. M. A Long-Range-Corrected Density Functional That Performs Well for Both Ground-State Properties and Time-Dependent Density Functional Theory Excitation Energies, Including Charge-Transfer Excited States. *The Journal of Chemical Physics* **2009**, *130* (5), 054112. <https://doi.org/10.1063/1.3073302>.
- (28) Chai, J.-D.; Head-Gordon, M. Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *The Journal of Chemical Physics* **2008**, *128* (8), 084106. <https://doi.org/10.1063/1.2834918>.
- (29) Pernal, K.; Podeszwa, R.; Patkowski, K.; Szalewicz, K. Dispersionless Density Functional Theory. *Phys. Rev. Lett.* **2009**, *103* (26), 263201. <https://doi.org/10.1103/PhysRevLett.103.263201>.
- (30) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. Development and Assessment of New Exchange–Correlation Functionals. *The Journal of Chemical Physics* **1998**, *109* (15), 6264–6271. <https://doi.org/10.1063/1.477267>.
- (31) Wilson, P. J.; Bradley, T. J.; Tozer, D. J. Hybrid Exchange–Correlation Functional Determined from Thermochemical Data and *Ab Initio* Potentials. *The Journal of Chemical Physics* **2001**, *115* (20), 9233–9242. <https://doi.org/10.1063/1.1412605>.
- (32) Keal, T. W.; Tozer, D. J. Semiempirical Hybrid Functional with Improved Performance in an Extensive Chemical Assessment. *The Journal of Chemical Physics* **2005**, *123* (12), 121103. <https://doi.org/10.1063/1.2061227>.
- (33) Adamson, R. D.; Gill, P. M. W.; Pople, J. A. Empirical Density Functionals. *Chemical Physics Letters* **1998**, *284* (1–2), 6–11. [https://doi.org/10.1016/S0009-2614\(97\)01282-7](https://doi.org/10.1016/S0009-2614(97)01282-7).
- (34) Lin, C. Y.; George, M. W.; Gill, P. M. W. EDF2: A Density Functional for Predicting Molecular Vibrational Frequencies. *Aust. J. Chem.* **2004**, *57* (4), 365. <https://doi.org/10.1071/CH03263>.

- (35) Van Voorhis, T.; Scuseria, G. E. A Novel Form for the Exchange-Correlation Energy Functional. *The Journal of Chemical Physics* **1998**, *109* (2), 400–410. <https://doi.org/10.1063/1.476577>.
- (36) Chachiyo, T.; Chachiyo, H. Understanding Electron Correlation Energy through Density Functional Theory. *Computational and Theoretical Chemistry* **2020**, *1172*, 112669. <https://doi.org/10.1016/j.comptc.2019.112669>.
- (37) Chachiyo, T.; Chachiyo, H. Simple and Accurate Exchange Energy for Density Functional Theory. *Molecules* **2020**, *25* (15), 3485. <https://doi.org/10.3390/molecules25153485>.
- (38) Verma, P.; Bartlett, R. J. Increasing the Applicability of Density Functional Theory. IV. Consequences of Ionization-Potential Improved Exchange-Correlation Potentials. *The Journal of Chemical Physics* **2014**, *140* (18), 18A534. <https://doi.org/10.1063/1.4871409>.
- (39) Jin, Y.; Bartlett, R. J. The QTP Family of Consistent Functionals and Potentials in Kohn-Sham Density Functional Theory. *The Journal of Chemical Physics* **2016**, *145* (3), 034107. <https://doi.org/10.1063/1.4955497>.
- (40) Haiduke, R. L. A.; Bartlett, R. J. Non-Empirical Exchange-Correlation Parameterizations Based on Exact Conditions from Correlated Orbital Theory. *The Journal of Chemical Physics* **2018**, *148* (18), 184106. <https://doi.org/10.1063/1.5025723>.
- (41) Jin, Y.; Bartlett, R. J. Accurate Computation of X-Ray Absorption Spectra with Ionization Potential Optimized Global Hybrid Functional. *The Journal of Chemical Physics* **2018**, *149* (6), 064111. <https://doi.org/10.1063/1.5038434>.
- (42) Sun, J.; Ruzsinszky, A.; Perdew, J. P. Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Phys. Rev. Lett.* **2015**, *115* (3), 036402. <https://doi.org/10.1103/PhysRevLett.115.036402>.
- (43) Bartók, A. P.; Yates, J. R. Regularized SCAN Functional. *J. Chem. Phys.* **2019**, *150* (16), 161101. <https://doi.org/10.1063/1.5094646>.
- (44) Furness, J. W.; Kaplan, A. D.; Ning, J.; Perdew, J. P.; Sun, J. Accurate and Numerically Efficient  $r^2$  SCAN Meta-Generalized Gradient Approximation. *J. Phys. Chem. Lett.* **2020**, *11* (19), 8208–8215. <https://doi.org/10.1021/acs.jpclett.0c02405>.
- (45) Dahlke, E. E.; Truhlar, D. G. Improved Density Functionals for Water. *J. Phys. Chem. B* **2005**, *109* (33), 15677–15683. <https://doi.org/10.1021/jp052436c>.
- (46) Yu, H. S.; Zhang, W.; Verma, P.; He, X.; Truhlar, D. G. Nonseparable Exchange–Correlation Functional for Molecules, Including Homogeneous Catalysis Involving Transition Metals. *Phys. Chem. Chem. Phys.* **2015**, *17* (18), 12146–12160. <https://doi.org/10.1039/C5CP01425E>.
- (47) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Exchange-Correlation Functional with Broad Accuracy for Metallic and Nonmetallic Compounds, Kinetics, and Noncovalent Interactions. *The Journal of Chemical Physics* **2005**, *123* (16), 161103. <https://doi.org/10.1063/1.2126975>.
- (48) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2006**, *2* (2), 364–382. <https://doi.org/10.1021/ct0502763>.
- (49) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor Chem Account* **2008**, *120* (1–3), 215–241. <https://doi.org/10.1007/s00214-007-0310-x>.
- (50) Zhao, Y.; Truhlar, D. G. Density Functional for Spectroscopy: No Long-Range Self-Interaction Error, Good Performance for Rydberg and Charge-Transfer States, and Better Performance on Average than B3LYP for Ground States. *J. Phys. Chem. A* **2006**, *110* (49), 13126–13130. <https://doi.org/10.1021/jp066479k>.

- (51) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *The Journal of Chemical Physics* **2006**, *125* (19), 194101. <https://doi.org/10.1063/1.2370993>.
- (52) Zhao, Y.; Truhlar, D. G. Exploring the Limit of Accuracy of the Global Hybrid Meta Density Functional for Main-Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2008**, *4* (11), 1849–1868. <https://doi.org/10.1021/ct800246v>.
- (53) Peverati, R.; Truhlar, D. G. Improving the Accuracy of Hybrid Meta-GGA Density Functionals by Range Separation. *J. Phys. Chem. Lett.* **2011**, *2* (21), 2810–2817. <https://doi.org/10.1021/jz201170d>.
- (54) Peverati, R.; Truhlar, D. G. M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics. *J. Phys. Chem. Lett.* **2012**, *3* (1), 117–124. <https://doi.org/10.1021/jz201525m>.
- (55) Peverati, R.; Truhlar, D. G. An Improved and Broadly Accurate Local Approximation to the Exchange–Correlation Density Functional: The MN12-L Functional for Electronic Structure Calculations in Chemistry and Physics. *Phys. Chem. Chem. Phys.* **2012**, *14* (38), 13171. <https://doi.org/10.1039/c2cp42025b>.
- (56) Peverati, R.; Truhlar, D. G. Screened-Exchange Density Functionals with Broad Accuracy for Chemistry and Solid-State Physics. *Phys. Chem. Chem. Phys.* **2012**, *14* (47), 16187. <https://doi.org/10.1039/c2cp42576a>.
- (57) Yu, H. S.; He, X.; Li, S. L.; Truhlar, D. G. MN15: A Kohn–Sham Global-Hybrid Exchange–Correlation Density Functional with Broad Accuracy for Multi-Reference and Single-Reference Systems and Noncovalent Interactions. *Chem. Sci.* **2016**, *7* (8), 5032–5051. <https://doi.org/10.1039/C6SC00705H>.
- (58) Yu, H. S.; He, X.; Truhlar, D. G. MN15-L: A New Local Exchange–Correlation Functional for Kohn–Sham Density Functional Theory with Broad Accuracy for Atoms, Molecules, and Solids. *J. Chem. Theory Comput.* **2016**, *12* (3), 1280–1293. <https://doi.org/10.1021/acs.jctc.5b01082>.
- (59) Peverati, R.; Truhlar, D. G. Exchange–Correlation Functional with Good Accuracy for Both Structural and Energetic Properties While Depending Only on the Density and Its Gradient. *J. Chem. Theory Comput.* **2012**, *8* (7), 2310–2319. <https://doi.org/10.1021/ct3002656>.
- (60) Peverati, R.; Truhlar, D. G. Communication: A Global Hybrid Generalized Gradient Approximation to the Exchange–Correlation Functional That Satisfies the Second-Order Density–Gradient Constraint and Has Broad Applicability in Chemistry. *J. Chem. Phys.* **2011**, *135* (19), 191102. <https://doi.org/10.1063/1.3663871>.
- (61) Wang, Y.; Verma, P.; Jin, X.; Truhlar, D. G.; He, X. Revised M06 Density Functional for Main-Group and Transition-Metal Chemistry. *Proc Natl Acad Sci USA* **2018**, *115* (41), 10257–10262. <https://doi.org/10.1073/pnas.1810421115>.
- (62) Wang, Y.; Jin, X.; Yu, H. S.; Truhlar, D. G.; He, X. Revised M06-L Functional for Improved Accuracy on Chemical Reaction Barrier Heights, Noncovalent Interactions, and Solid-State Physics. *Proc Natl Acad Sci USA* **2017**, *114* (32), 8487–8492. <https://doi.org/10.1073/pnas.1705670114>.
- (63) Verma, P.; Wang, Y.; Ghosh, S.; He, X.; Truhlar, D. G. Revised M11 Exchange–Correlation Functional for Electronic Excitation Energies and Ground-State Properties. *J. Phys. Chem. A* **2019**, *123* (13), 2966–2990. <https://doi.org/10.1021/acs.jpca.8b11499>.
- (64) Verma, P.; Truhlar, D. G. HLE16: A Local Kohn–Sham Gradient Approximation with Good Performance for Semiconductor Band Gaps and Molecular Excitation Energies. *J. Phys. Chem. Lett.* **2017**, *8* (2), 380–387. <https://doi.org/10.1021/acs.jpcllett.6b02757>.

- (65) Verma, P.; Truhlar, D. G. HLE17: An Improved Local Exchange–Correlation Functional for Computing Semiconductor Band Gaps and Molecular Excitation Energies. *J. Phys. Chem. C* **2017**, *121* (13), 7144–7154. <https://doi.org/10.1021/acs.jpcc.7b01066>.
- (66) Menconi, G.; Wilson, P. J.; Tozer, D. J. Emphasizing the Exchange–Correlation Potential in Functional Development. *The Journal of Chemical Physics* **2001**, *114* (9), 3958–3967. <https://doi.org/10.1063/1.1342776>.