

# Is the Accuracy of Density Functional Theory for Atomization Energies and Densities in Bonding Regions Correlated?

Kurt Brorsen

PI: Sharon Hammes-Schiffer

University of Illinois at Urbana-Champaign

# Density Functional Theory (DFT)

- Electronic Schrödinger equation

$$H_{\text{elec}} \Psi_{\text{elec}}(\mathbf{r}^e; \mathbf{r}^p) = E_{\text{elec}}(\mathbf{r}^p) \Psi_{\text{elec}}(\mathbf{r}^e; \mathbf{r}^p)$$

$$H_{\text{elec}} = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_A^{N_p} \frac{Z_A}{|\mathbf{r}_i^e - \mathbf{r}_A^p|} + \sum_{i>j}^{N_e} \frac{1}{|\mathbf{r}_i^e - \mathbf{r}_j^e|}$$

- Wave function of  $3N_e$  variables
- Difficult to solve
- Hohenberg-Kohn theorem
  - The external potential,  $V_{\text{ext}}$ , is uniquely determined by the ground-state electronic density,  $n(\mathbf{r})$ , a function of three variables
  - The energy is a functional of the density.

# Kohn-Sham Formalism of DFT

- Fock-like equations of a non-interacting system

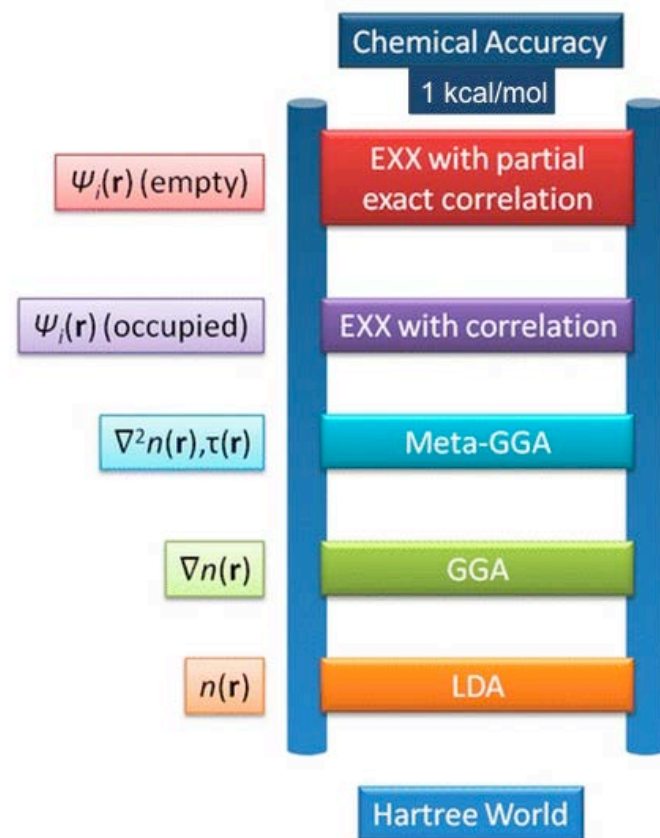
$$\left( -\frac{1}{2}\nabla^2 + v_{\text{ext}} + U + v_{\text{xc}} \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

- First three terms are easy
  - Non-interacting kinetic energy
  - External potential
  - Hartree potential
- $v_{\text{xc}}$ , the exchange-correlation potential, is unknown and must be approximated

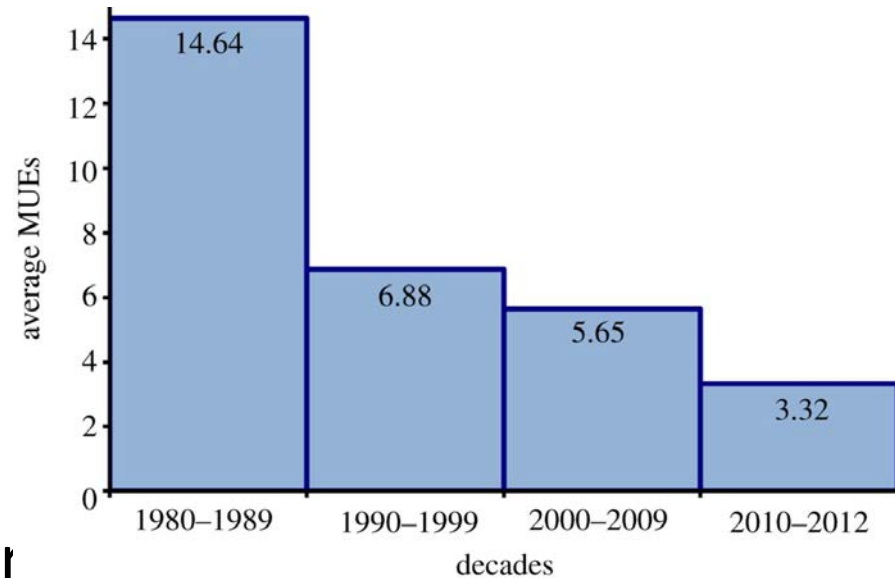
# Exchange-Correlation Functional

- Jacob's ladder
  - LDA, GGA, mGGA, hGGA, dhGGA
- How to develop functionals?
  - Perdew school
    - Using physical constraints and properties of exact functional
      - SVWN, PBE, TPSS, SCAN, etc.
    - “In DFT, for a very smart person, it’s very difficult to do anything.” – Mike Pak 4/19/2016, UIUC
  - Truhlar school
    - Parameterization and fitting against empirical data
      - Minnesota functionals, Head-Gordon functionals
    - Has increasingly come to dominate functional development



# Exchange-Correlation Functional

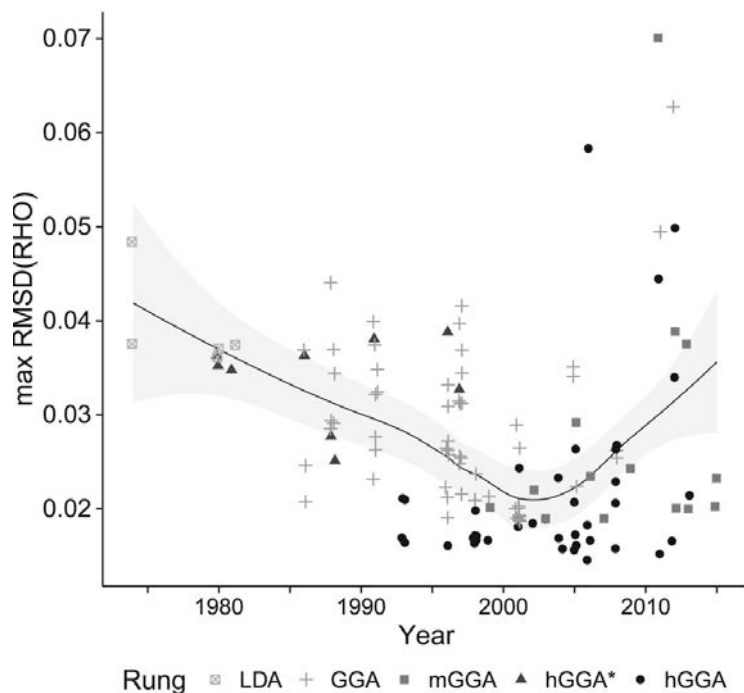
- Functional developments has typically focused on improved energies
  - Exceptions B97-1, HCTC functionals
- Exact functional should give exact density as well as exact energy
- Recent study (Medvedev et al. *Science* 355 **2017**) has called into question whether functional development has “strayed” from the path of the exact functional



Peverati, Truhlar, *Phil. Trans. Roy. Soc. Lon. A* 372 **2014**

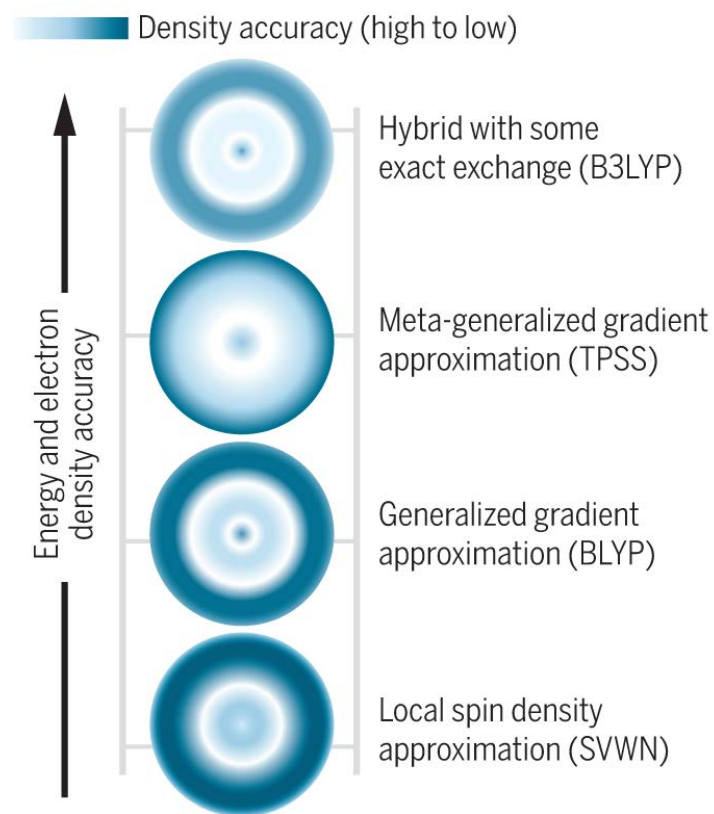
# Atomic densities for DFT

- Densities for atoms have gotten worse since early 2000s for atomic systems in parallel with the rise of highly parameterized functionals



Medvedev et al. *Science* 355 2017

Test calculations showing correct trend:



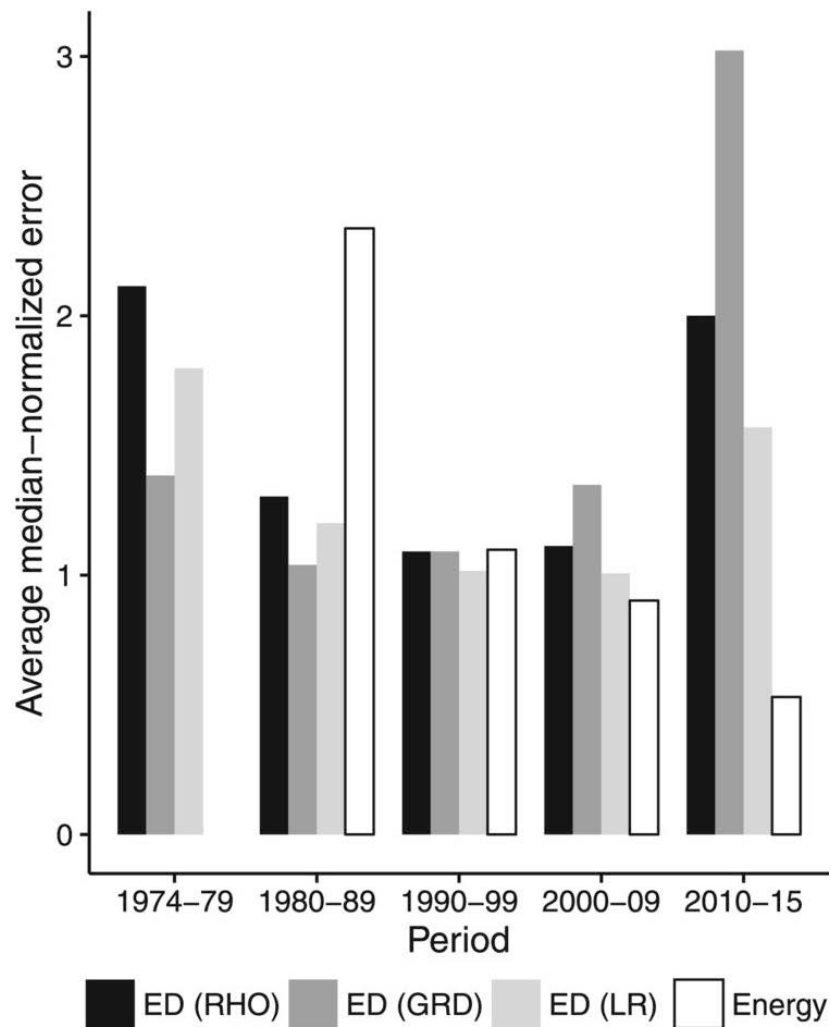
Hammes-Schiffer *Science* 355 2017

# List of density errors for atomic systems

Best Performing				Worst Performing			
Method	Rung	Year	Max NE	Method	Rung	Year	Max NE
mPW3PBE	hGGA	1998	1.778	M11-L	mGGA	2011	15.316
APFD	hGGA	2012	1.813	MN12-SX	hGGA	2012	13.005
B3PW91	hGGA	1993	1.816	M11	hGGA	2011	10.191
PBE0	hGGA	1999	1.818	MN12-L	mGGA	2012	8.995
B98	hGGA	1998	1.826	M05	hGGA	2005	7.652
BHHLYP	hGGA	1993	1.851	N12-SX	hGGA	2012	6.970
B97-3	hGGA	2005	1.883	N12	GGA	2012	6.709
mPW1PBE	hGGA	1998	1.910	M06-HF	hGGA	2006	6.125
B3P86	hGGA	1993	1.937	M06	hGGA	2006	5.420
O3LYP	hGGA	2001	1.947	SOGGA11	GGA	2011	4.971
PBE1KCIS	hGGA	2005	1.954	M08-HX	hGGA	2008	4.88
mPW1PW91	hGGA	1998	1.955	SLATER	LDA	1974	4.864
B97-1	hGGA	1998	1.962	M08-SO	hGGA	2008	4.676
HSE06	hGGA	2006	1.982	SLYP	GGA	1988	4.429
PBEh1PBE	hGGA	1998	1.983	SOP	GGA	1997	4.182
B97-2	hGGA	2001	2.018	M06-2X	hGGA	2006	4.027
B1B95	hGGA	1996	2.033	SPW91	GGA	1991	3.989
TPSS	mGGA	2003	2.042	SPZ81	LDA	1981	3.985
TPSSh	hGGA	2003	2.045	SVWN	LDA	1980	3.984
TPSSm	mGGA	2007	2.077	SPBE	GGA	1997	3.978
X3LYP	hGGA	2005	2.084	SVWN1RPA	LDA	1980	3.977
SCAN	mGGA	2015	2.107	M06-L	mGGA	2006	3.974
B3LYP	hGGA	1993	2.123	SP86	GGA	1986	3.821
				X $\alpha$	LDA	1974	3.777

# Extending the previous study

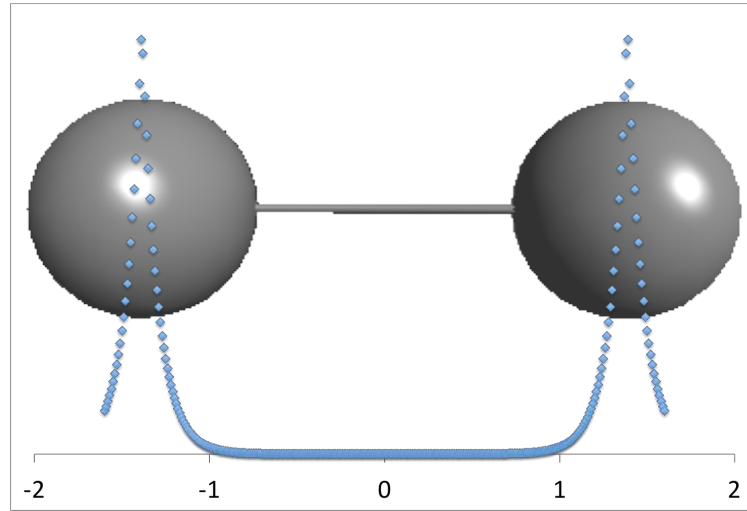
- Look at molecules not atoms
  - Highly charged atoms not similar to typical chemical systems
  - Modern functionals might give good density in the “bonding region”
- Use consistent energy metric
  - Study used molecular energies, but atomic densities
  - Maybe atomic energy errors didn't get better?
- Focus on a single density error metric





# Density of molecules

- 14 closed shell diatomics
- Smaller test set of functionals
- Error metrics



- Density Error
- Mean absolute atomization energy error (MAAEE)

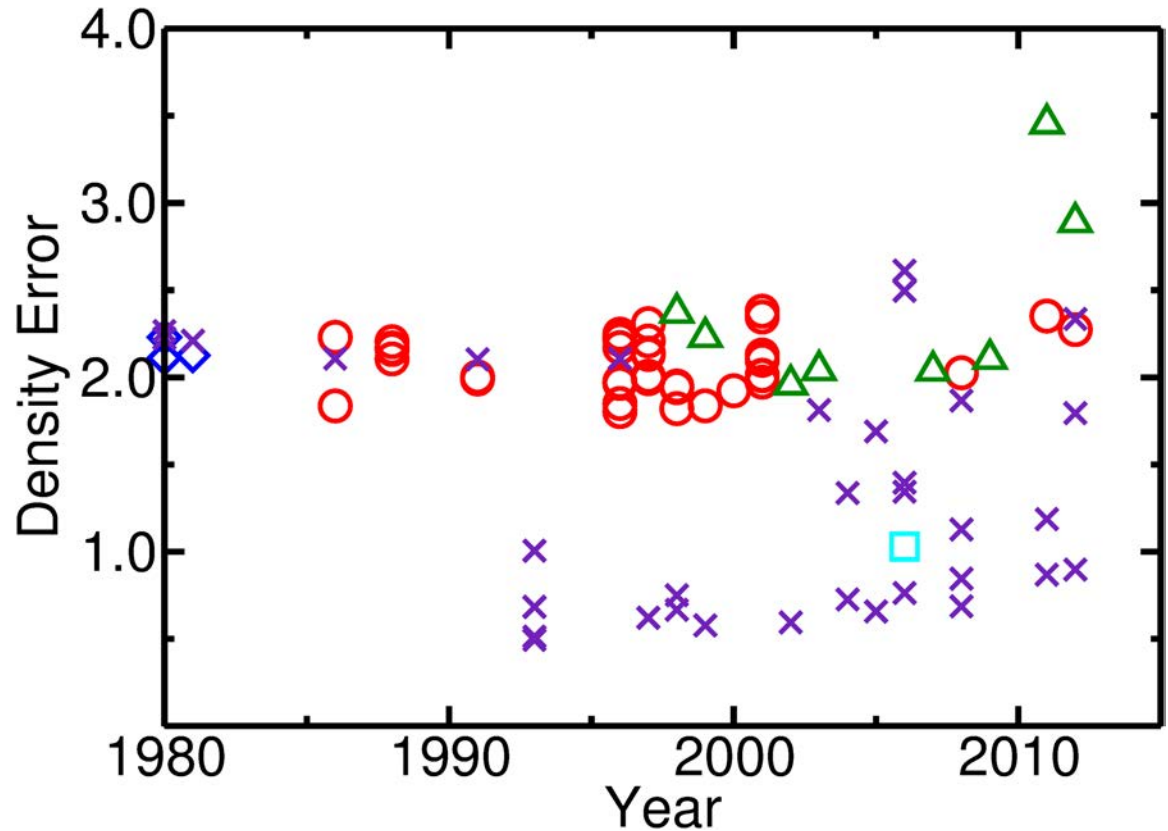
$$\text{RMSD}_{\text{on,functional,molecule}} = \sqrt{\frac{1}{N_{\text{on}}} \sum_i^{N_{\text{on}}} \left( n_i^{\text{CCSD,molecule}} - n_i^{\text{functional,molecule}} \right)^2}$$

$$\text{Density\_Error}^{\text{functional}} = \frac{\text{RMSD}_{\text{off,functional}}}{\text{median}\{\text{RMSD}_{\text{off,functionals}}\}} + \frac{\text{RMSD}_{\text{on,functional}}}{\text{median}\{\text{RMSD}_{\text{on,functionals}}\}}$$

$$\text{MAAEE}^{\text{functional}} = \frac{1}{N_{\text{mol}}} \sum_j^{N_{\text{mol}}} \left| E_{\text{atomization}}^{\text{CCSD}} - E_{\text{atomization}}^{\text{functional}} \right|$$

# Year vs. Density Error

- Slight upward trend beginning in the early 2000s
- Less pronounced than atomic data
  - Due to different measure of density error



◇ LDA    ○ GGA    △ mGGA    × hGGA    □ dhGGA

# List of density errors for molecular systems

## Best functionals

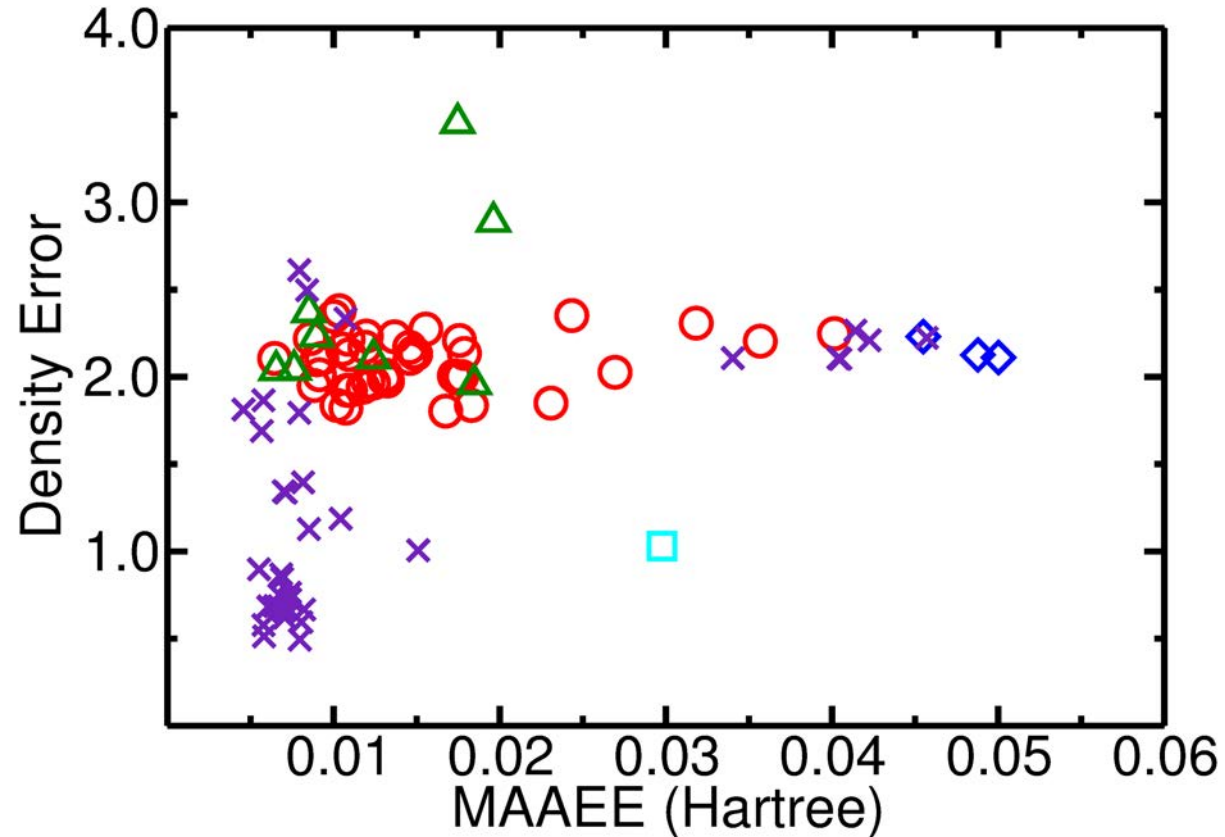
Functional	Year	Type	Density Error
B3P86	1993	hGGA	0.494
B3PW91	1993	hGGA	0.512
PBE0	1999	hGGA	0.577
tHCTHhyb	2002	hGGA	0.594
B97	1997	hGGA	0.621
B97-3	2005	hGGA	0.657
B97-1	1998	hGGA	0.666
B3LYP	1993	hGGA	0.683
B3LYPV3	1993	hGGA	0.683
B3LYPV1R	1993	hGGA	0.684
X3LYP	2008	hGGA	0.686
CAMB3LYP	2004	hGGA	0.726
B98	1998	hGGA	0.750
M06-2X	2006	hGGA	0.763
wB97X	2008	hGGA	0.845
SOGGA11X	2011	hGGA	0.868
APFD	2012	hGGA	0.897
BHHLYP	1993	hGGA	1.006
B2PLYP	2006	dhGGA	1.029
wB97	2008	hGGA	1.127

## Worst Functionals

Functional	Year	Type	Density Error
M11-L	2011	mGGA	3.455
MN12-L	2012	mGGA	2.889
M06-L	2006	mGGA	2.612
M06-HF	2006	hGGA	2.496
OPBE	2001	GGA	2.379
VS98	1998	mGGA	2.370
SOGGA11	2011	GGA	2.352
OPW91	2001	GGA	2.346
MN12SX	2012	hGGA	2.335
PBEX	1997	GGA	2.308
N12	2012	GGA	2.273
VWN1RPA	1980	hGGA*	2.265
GILL	1996	GGA	2.248
GVWN1RPA	1996	GGA	2.234
PKZB	1999	mGGA	2.231
SVWN	1980	LDA	2.231
OP86	1986	GGA	2.230
VWN5	1980	hGGA*	2.223
GVWN	1996	GGA	2.220
GPZ81	1996	GGA	2.215

# Atomization Energy vs. Density

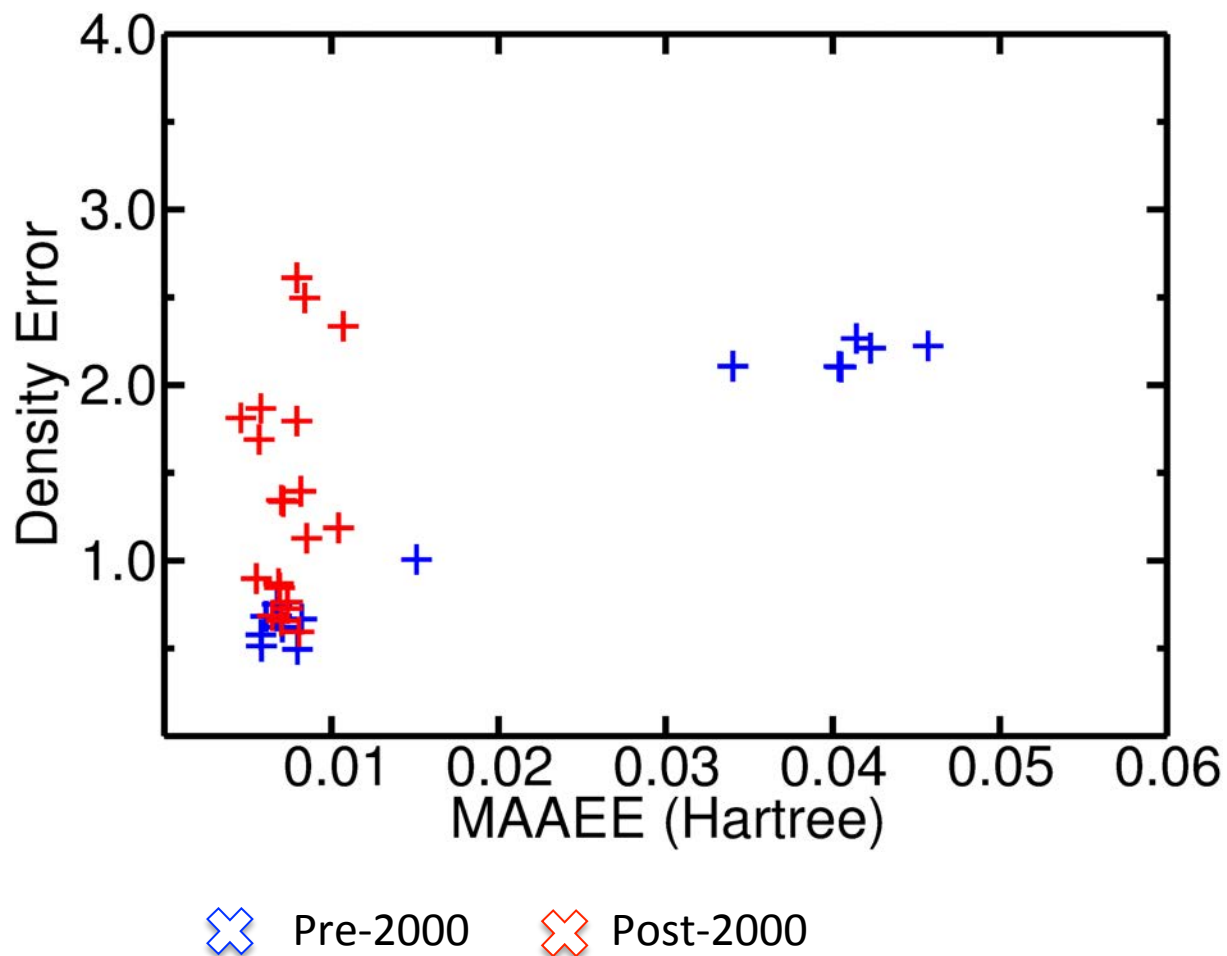
- No correlation for LDA, GGA, or dhGGA
  - But no variance in density error
- Positive Correlation for mGGA
- No correlation for hGGA
  - With variance in density error



◇ LDA   ○ GGA   △ mGGA   × hGGA   □ dhGGA

# MAAEE vs. Density for hGGAs

- Sort hGGA type functionals by year developed
- Clear change in the early 2000s
  - Sacrificed density for other properties



# Conclusions/Acknowledgements

- Agreement with previous atomic results
  - Densities have gotten worse since the early 2000s
  - Decoupling of diatomic density errors and atomization energy errors for hGGA type functionals starting in early 2000s
- Future
  - Could be interesting to look at bonds in larger molecules?
- University of Illinois
  - Yang Yang, Mike Pak, Sharon Hammes-Schiffer

