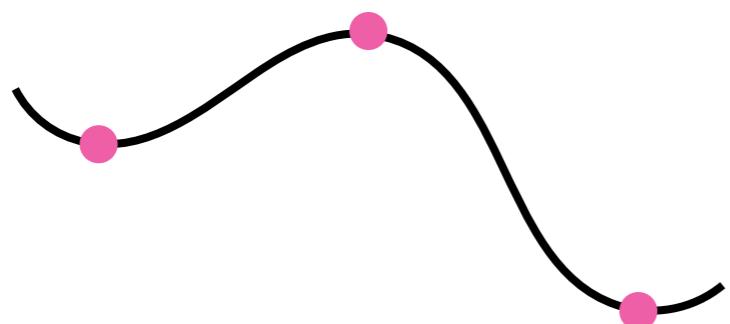


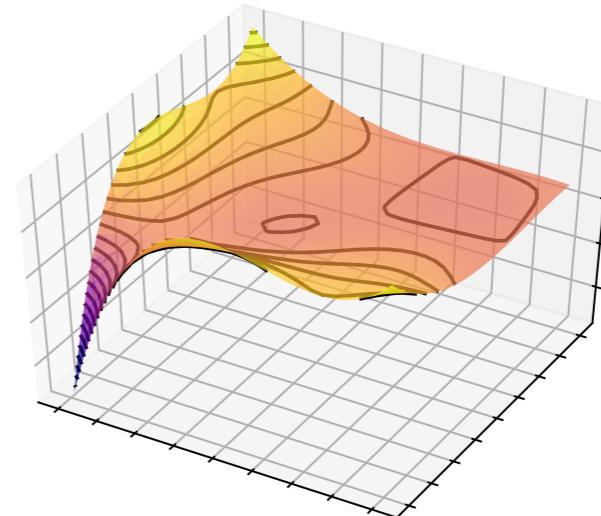
DFT: Implementation and Effective Usage

Tom Young
25th March 2020

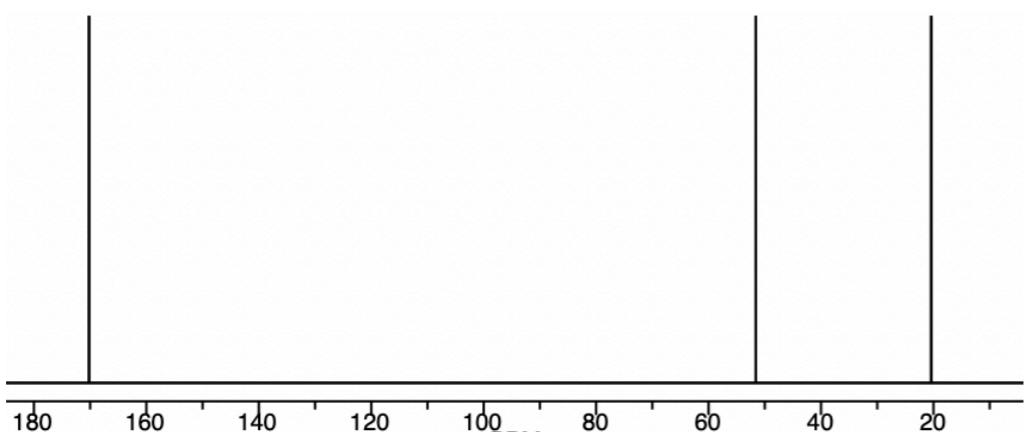
Motivation



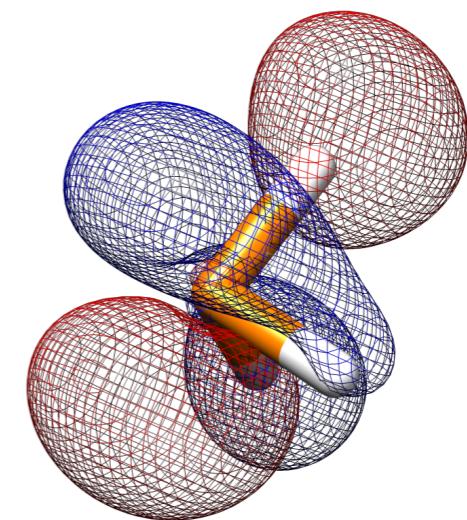
Kinetics and
thermodynamics



Classical/quantum
dynamics

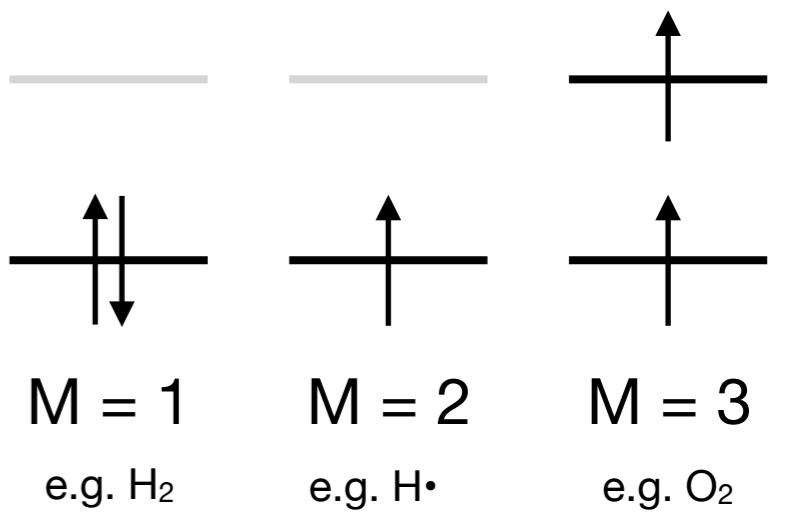
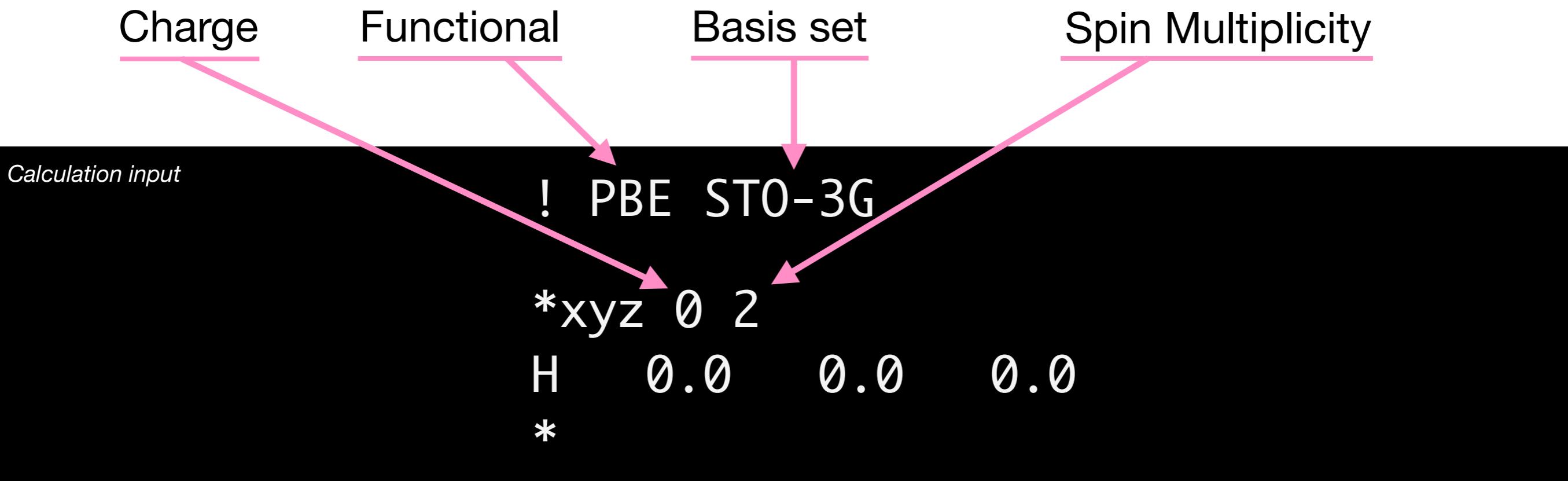


Spectra (NMR, IR, UV, etc.)



Orbital analysis

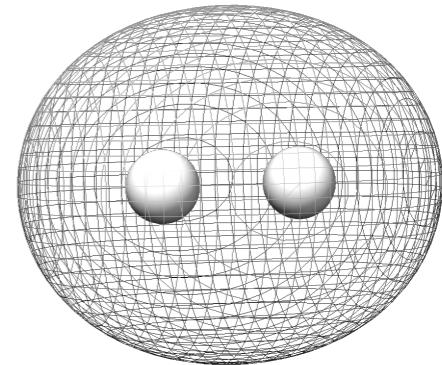
Hydrogen atom



KS Functional

$$E[\rho] = T_{exact}[\rho] + V_{ne}[\rho] + V_{ee}[\rho] + E_{ex}[\rho] + E_c[\rho]$$

$$\rho(x, y, z) \approx \sum_{i \in elec} |\varphi(i)|^2$$



$$\rho \approx |\varphi_{\sigma_g}(1)|^2 + |\varphi_{\sigma_g}(2)|^2$$

KS Functional

$$E[\rho] = T_{exact}[\rho] + V_{ne}[\rho] + V_{ee}[\rho] + E_{ex}[\rho] + E_c[\rho]$$

Calculation output

Exchange Functional	Exchange PBE
PBE kappa parameter	XKappa 0.804000
PBE mue parameter	XMuePBE 0.219520
Correlation Functional	Correlation PBE
PBE beta parameter	CBetaPBE 0.066725
LDA part of GGA corr.	LDAOpt PW91-LDA
.....

Specific to PBE functional:

$$E_{ex}[\rho] = \int_{all} f(\rho, \nabla \rho, \kappa, \mu) dr$$

Recovers many exact properties of ρ in limiting regimes

KS Functional

$$E[\rho] = T_{exact}[\rho] + V_{ne}[\rho] + V_{ee}[\rho] + E_{ex}[\rho] + E_c[\rho]$$

Calculation output

Exchange Functional	Exchange PBE
PBE kappa parameter	XKappa 0.804000
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Correlation Functional	Correlation PBE
PBE beta parameter	CBetaPBE 0.066725
LDA part of GGA corr.	LDAOpt PW91-LDA
.....

Specific to PBE functional:

$$E_c[\rho] = \int_{all} f(\rho, \nabla \rho, \beta) dr$$

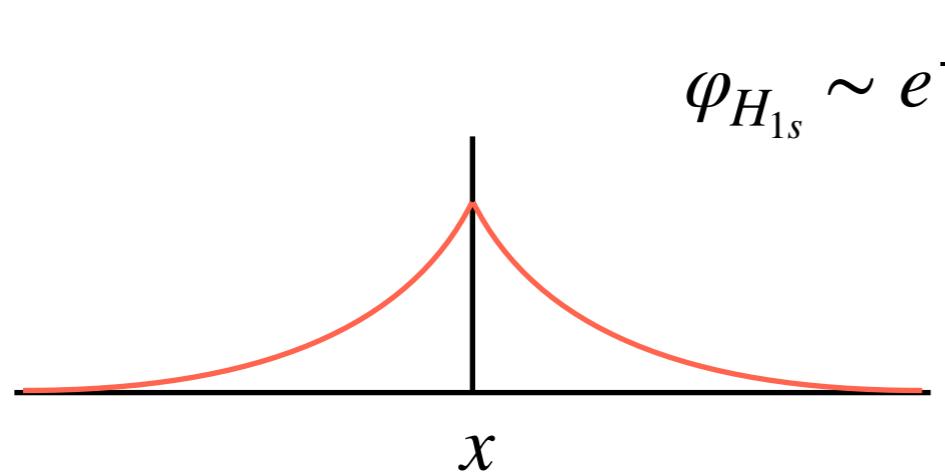
Basis set

Need an ansatz for molecular orbitals \Rightarrow LCAO

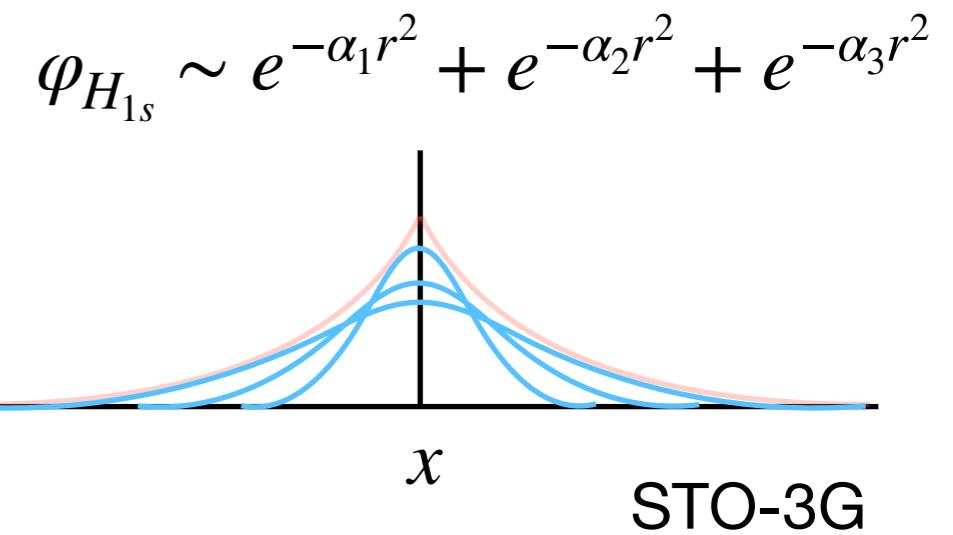
$$\varphi_{orb} = ??$$

$$\varphi_{orb} = \sum_n c_n \varphi_n^{AO}$$

Integrals are expensive to evaluate with $\exp(-r) \Rightarrow \exp(-r^2)$



\approx



Split valence basis set

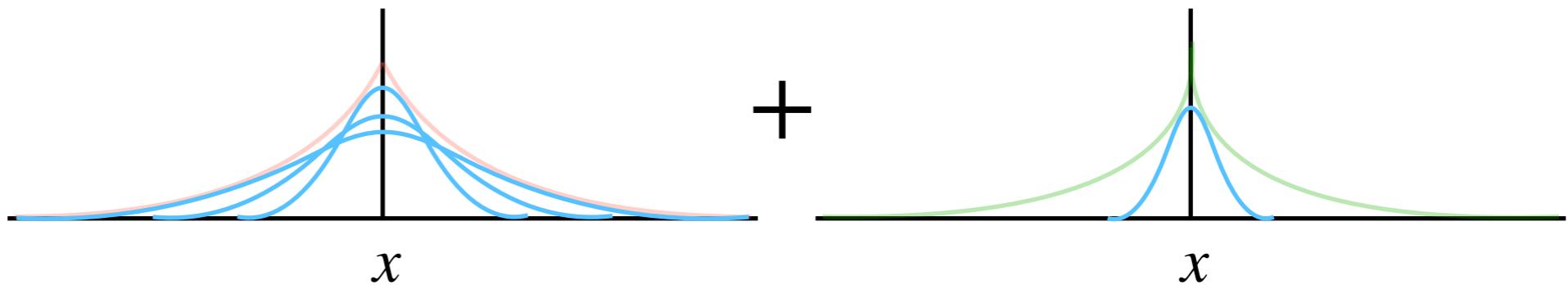
Core orbitals:
6 primitives

6-31G

Valence
orbitals:

& def2-SVP etc.

$$\varphi_{val} \sim e^{-\zeta_1 r} + e^{-\zeta_2 r}$$



AOs of many electron atoms are not fully hydrogenic

Basis set contraction

STO-3G: 3 primitive gaussians for each AO

Calculation output

# of primitive gaussian shells	...	3
# of primitive gaussian functions	...	3
# of contracted shells	...	1
# of contracted basis functions	...	1
Highest angular momentum	...	0

:

:

Contracted basis function \Leftrightarrow basis function

$$c_1 e^{-\alpha_1 r^2} + c_2 e^{-\alpha_2 r^2} + c_3 e^{-\alpha_3 r^2} \xrightarrow[\text{(3s) } \rightarrow [2s]]{\text{contraction}} c_a (k_1 e^{-\alpha_1 r^2} + k_2 e^{-\alpha_2 r^2}) + c_3 e^{-\alpha_3 r^2}$$

SCF

The energy depends on the density but the '**best**' density is not a priori known*, thus need to guess MO coefficients & iterate to convergence

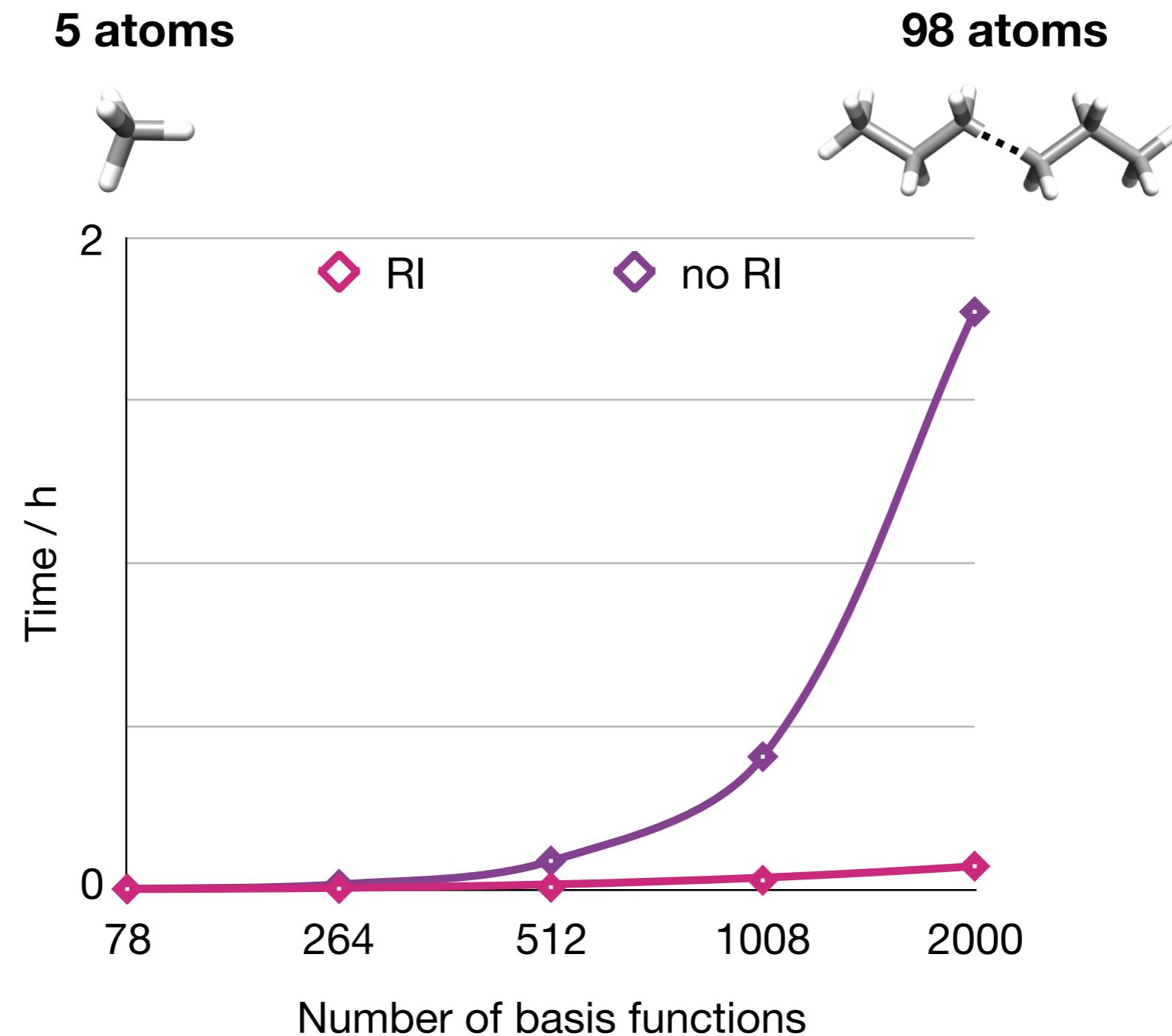
Calculation output

```
-----  
SCF ITERATIONS  
-----  
ITER      Energy       Delta-E       Max-DP       RMS-DP      [F,P]      Damp  
        *** Starting incremental Fock matrix formation ***  
0       -0.4643763929  0.000000000000 0.00000000 0.00000000 0.00000000 0.7000  
        **** Energy Check signals convergence ***  
-----
```

:

:

Resolution of Identity



$O(N^4) \rightarrow O(N^3)^*$ & small prefactor

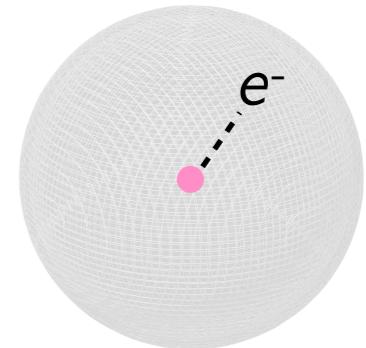
RI is on by default in ORCA, but only for ‘pure’ (GGA) functionals

```
! PBE def2-SVP
```

RI with hybrids possible with COSX

```
! PBE0 RIJCOSX def2-SVP
```

Auxiliary basis needs to be *much* larger than the core basis set. ORCA defaults are selected automatically and highly recommended



$$E_{\text{exact}} = -0.5 \text{ Ha}$$

$E(\text{M06-2X})$: -0.4988... Ha

$E(\text{PBE})$: -0.4999... Ha

$E(\text{PBE0})$: -0.5012... Ha

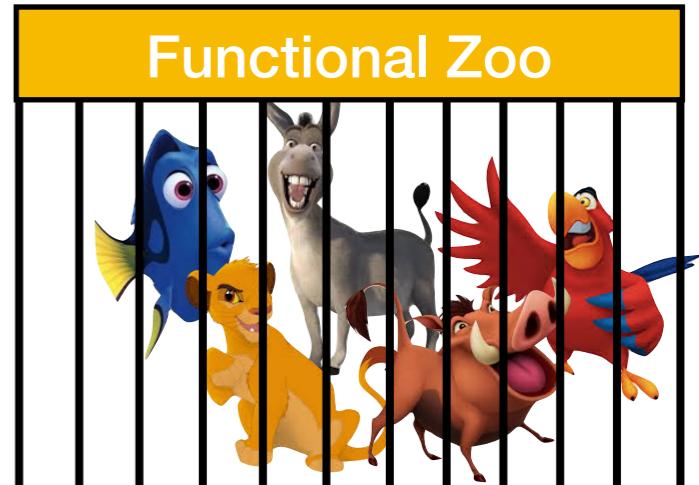
PBE is best? PBE0 violates the variational principle?

Some other general advice

Functional:

PBE0: 0–200 atoms

PBE: 200+ atoms
(ω B97X-D3)



Dispersion:

D3BJ

Basis set:

def2-SVP: Optimisation

def2-TZVP: Single point

(ma)- : Radicals and anions

What accuracy do you need?

PBE0/def2-TZVP//PBE0/def2-SVP

Single point

Optimisation

$$E[\rho] = \underline{T_{exact}[\rho]} + V_{ne}[\rho] + V_{ee}[\rho] + E_{ex}[\rho] + E_c[\rho]$$

Exact KE of **non-interacting**
electrons:

$$T_{exact}[\rho] = -\frac{1}{2} \sum_{i \in elec} \int_{all} \varphi^*(i) \nabla^2 \varphi(i) d\mathbf{r}$$

KS Functional

$$E[\rho] = T_{exact}[\rho] + \underline{V_{ne}[\rho]} + V_{ee}[\rho] + E_{ex}[\rho] + E_c[\rho]$$

$$V_{ne}[\rho] = - \sum_{A \in nuc} \sum_{i \in elec} \int_{all} \frac{Z_A \varphi^*(i) \varphi(i)}{|R_A - \mathbf{r}_i|} d\mathbf{r}$$

KS Functional

$$E[\rho] = T_{exact}[\rho] + V_{ne}[\rho] + \underline{V_{ee}[\rho]} + E_{ex}[\rho] + E_c[\rho]$$

$$V_{ee}[\rho] = \sum_{i \in elec} \sum_{j > i} \int_{all} \frac{|\varphi(i)|^2 |\varphi(j)|^2}{|r_i - r_j|} dr$$