



Evans boldly put 50 atm of ethylene in a cell with 25 atm of oxygen. The apparatus subsequently blew up, but luckily not before he had obtained the spectra shown in Figure 8.

*A.J. Mehrer and R.S. Mulliken,  
Chem. Rev. 69 (1969) 639-656*

## Practical Quantum Chemistry, L3: Methods and terminology, part C

*coupled cluster theory, densities, density functional theory,  
exchange-correlation functionals, long-range corrections in DFT*

Prof Ilya Kuprov, Weizmann Institute of Science, 2025

For all lecture notes and video records see <https://spindynamics.org>

# Coupled-cluster theory

Configuration interaction was *summing* over all single, double, *etc.* excitations:

$$\Psi = \frac{\text{diagram 1}}{\text{diagram 2}} + \sum_{\text{diagram 3}} \frac{\text{diagram 4}}{\text{diagram 5}} + \sum_{\text{diagram 6}} \frac{\text{diagram 7}}{\text{diagram 8}} + \dots$$

But algebraically:

$$\Psi = \hat{\Omega} \Phi_0$$

Annotations:

- $\hat{\Omega}$ : unitary operator
- $\Phi_0$ : Hartree-Fock ground state
- $\Psi$ : exact solution

By group theory, there must exist an exponential map from a generator algebra:

$$\exists \hat{T}, \quad \hat{\Omega} = \exp(\hat{T}) = 1 + \hat{T} + \hat{T}^2/2 + \hat{T}^3/6 + \dots, \quad \hat{T} = \underbrace{\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots}_{\text{generators}}$$

Annotations:

- $\hat{\Omega}$ : unitary
- $\hat{T}$ : skew-Hermitian

whose basis operators are then single, double, *etc.* excitations:

$$\begin{aligned} \hat{T}_1 \Phi_0 &= \sum_{i,a} t_i^a \Phi_i^a, & \hat{T}_2 \Phi_0 &= \sum_{i>j, a>b} t_{ij}^{ab} \Phi_{ij}^{ab}, & \hat{T}_2^2 \Phi_0 &= \sum_{\substack{i>j, k>l \\ a>b, c>d}} t_{ij}^{ab} t_{kl}^{cd} \Phi_{ijkl}^{abcd} \\ &\uparrow & \uparrow & & & \\ &\text{adjustable} & \text{adjustable} & & & \\ &\text{parameters} & \text{parameters} & & & \\ \hat{T}_1 \hat{T}_2 \Phi_0 &= \sum_{i, a, k>l, c>d} t_i^a t_{kl}^{cd} \Phi_{ikl}^{acd} \end{aligned}$$

Annotations:

- $t_i^a, t_{ij}^{ab}, t_{kl}^{cd}, t_{ikl}^{acd}$ : adjustable parameters
- Structure relations of the algebra

A better formulation of configuration interaction!

# Coupled-cluster theory

| Method              | RMS bond length error,<br>(Angstrom from XRD) |
|---------------------|-----------------------------------------------|
| HF/6-31G(d,p)       | 0.021                                         |
| HF/6-311G(d,p)      | 0.022                                         |
| MP2/6-31G(d,p)      | 0.014                                         |
| MP2/6-311G(d,p)     | 0.014                                         |
| QCISD/6-311G(d,p)   | 0.013                                         |
| CCSD(T)/6-311G(d,p) | 0.013                                         |

| Method                | RMS atomization energy error,<br>(kcal/mol from experiment) |
|-----------------------|-------------------------------------------------------------|
| HF/6-31G(d)           | 85.9                                                        |
| HF/6-311G(2df,p)      | 82.0                                                        |
| MP2/6-31G(d)          | 22.4                                                        |
| MP2/6-311G(d,p)       | 23.7                                                        |
| QCISD/6-311G(d)       | 28.8                                                        |
| CCSD(T)/6-311G(2df,p) | 11.5                                                        |

| Method  | $E_{\text{CC}} - E_{\text{FCI}}$ for water in<br>cc-pVDZ, Hartree |
|---------|-------------------------------------------------------------------|
| RHF     | 0.217822                                                          |
| CCSD    | 0.003744                                                          |
| CCSDT   | 0.000493                                                          |
| CCSDTQ  | 0.000019                                                          |
| CCSDTQP | 0.000003                                                          |

CC is size-consistent:

$$E_{\text{CC}}(1+2) = E_{\text{CC}}(1) + E_{\text{CC}}(2)$$

| Method  | Complexity scaling |
|---------|--------------------|
| CCD     | $O(n^6)$           |
| CCSD    | $O(n^6)$           |
| CCSD(T) | $O(n^7)$           |

# Summary of post-HF methods

Single reference methods are accurate *if and only if* the HF reference state is a good starting point.

In systems with homolytic bond cleavage or degeneracies, MP $n$ , CI, and CC will fail – use multi-reference methods.

| Method | E <sub>corr</sub> (Be) | Method | E <sub>corr</sub> (Be) | Method  | E <sub>corr</sub> (Be) |
|--------|------------------------|--------|------------------------|---------|------------------------|
| MP2    | 67.85%                 |        |                        |         |                        |
| MP3    | 86.90%                 | CISD   | 96.05%                 | CCSD    | 99.75%                 |
| MP4    | 94.58%                 |        |                        | CCSD(T) | 99.99%                 |
| MP5    | 98.15%                 | CISDT  | 96.29%                 | CCSDT   | 99.99%                 |
| MP6    | 99.64%                 |        |                        |         |                        |
| MP7    | 100.15%                | CISDTQ | 100%                   | CCSDTQ  | 100%                   |

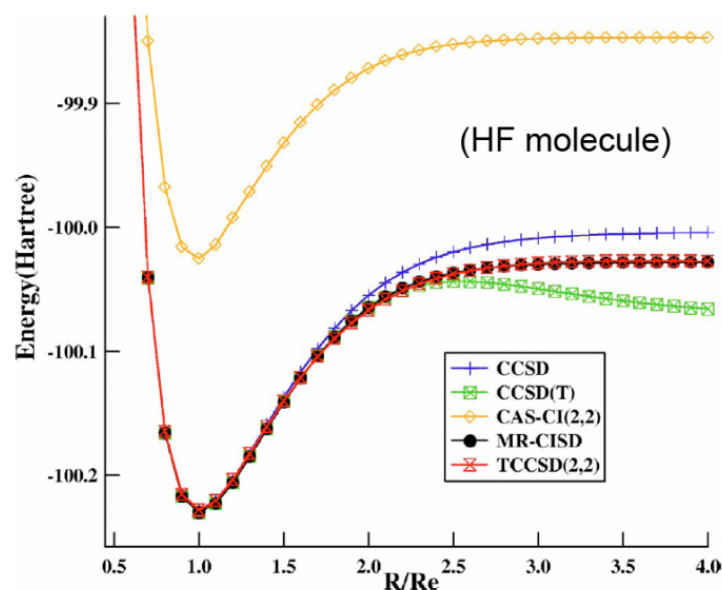


**TABLE 1: RHF, B3LYP, MP2, and CISD Fully Optimized Geometries and the Experimental Values of the Product CpCo(N(O)CH<sub>3</sub>)PH<sub>3</sub> (4)**

|           | RHF   | DFT   | MP2   | CISD  | expt  |
|-----------|-------|-------|-------|-------|-------|
| Co–Cp     | 2.076 | 1.849 | 1.731 | 1.888 | 1.718 |
| Co–P      | 2.511 | 2.287 | 2.164 | 2.360 | 2.174 |
| Co–N      | 1.991 | 1.772 | 1.711 | 1.787 | 1.780 |
| N–O       | 1.226 | 1.324 | 1.378 | 1.295 | 1.282 |
| N–C       | 1.487 | 1.514 | 1.527 | 1.504 | 1.484 |
| P–Co–N    | 96.8  | 95.8  | 94.4  | 96.0  | 92.4  |
| Co–N–O    | 124.2 | 126.4 | 128.3 | 125.4 | 125.6 |
| Co–N–C    | 121.2 | 123.5 | 124.5 | 123.5 | 124.4 |
| ave % dev | 7.65  | 2.95  | 2.48  | 3.25  |       |

# Summary of post-HF methods

| Methods<br>(without basis<br>screening) | Scaling with the<br>number of basis<br>functions |
|-----------------------------------------|--------------------------------------------------|
| HF                                      | $O(n^4)$                                         |
| MP2                                     | $O(n^5)$                                         |
| MP3, CISD,<br>CCSD,<br>QCISD            | $O(n^6)$                                         |
| MP4,<br>CCSD(T),<br>QCISD(T)            | $O(n^7)$                                         |
| MP5, CISDT,<br>CCSDT                    | $O(n^8)$                                         |
| MP6                                     | $O(n^9)$                                         |
| MP7,<br>CISDTQ,<br>CCSDTQ               | $O(n^{10})$                                      |
| FCI                                     | $O(n!)$                                          |

## Hartree-Fock:

- Up to a few hundred atoms.
- First and second analytical derivatives readily available with respect to common perturbations.

## MP2, MP4:

- Efficient implementations scale to ~100 atoms for MP2 and to ~20 atoms for MP4.
- First and second analytical derivatives readily available with respect to common perturbations for MP2, numerical derivatives only for MP4.

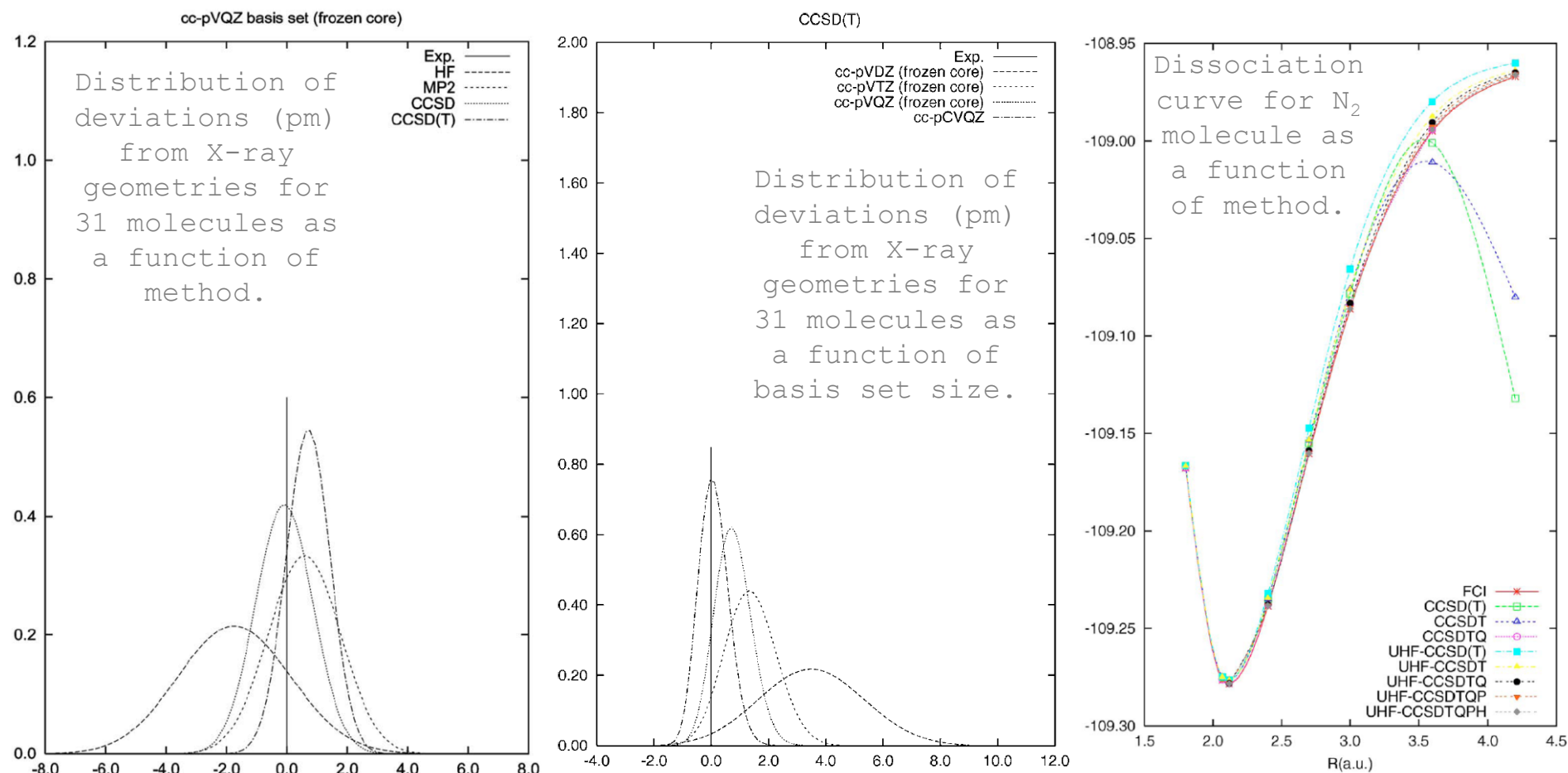
## CISD, CCSD:

- Efficient implementations scale to ~20 atoms.
- First analytical derivatives usually available, second derivatives mostly numerical for now.

## FCI:

- 3-4 simple atoms at most.
- All derivatives numerical.

# Summary of post-HF methods



For properties other than energy, a higher level method does not necessarily mean a more accurate answer – beware of error compensation situations.

# Summary of post-HF methods

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Fast approximate methods (but capturing the essentials):

**HF/6-31G(d,p) or HF/cc-pVDZ**

Slow accurate methods:

**MP2/6-311G(2d,2p) or MP2/cc-pVTZ**

Very slow, very accurate methods:

**CCSD(T)/cc-pVQZ and higher**

Specialized high-accuracy compound methods:

**MP2-R12, G1-G3, G2MP2, G3MP2 etc.**



Energies (but not usually other parameters) can be extrapolated to the *basis set limit* – effectively to the complete basis set. Dunning-Feller extrapolation scheme is given below, in which  $n$  is the zeta index of an (aug-)cc-pV $n$ Z basis set:

$$E_n = E_{\text{CBS}} + \alpha e^{-\beta n}$$

# Densities and distributions

*Density* refers to a continuous spatial distribution of a certain property. Commonly encountered densities of chemical interest are:

Probability density

$$p(x, y, z) = |\psi(x, y, z)|^2$$

Electron density

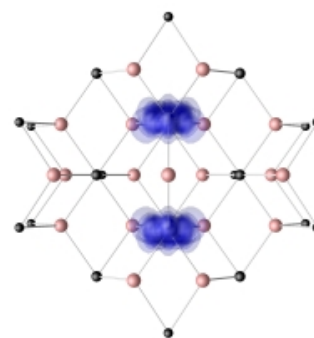
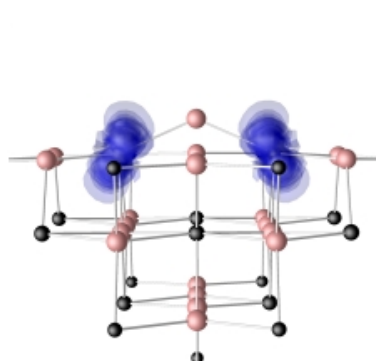
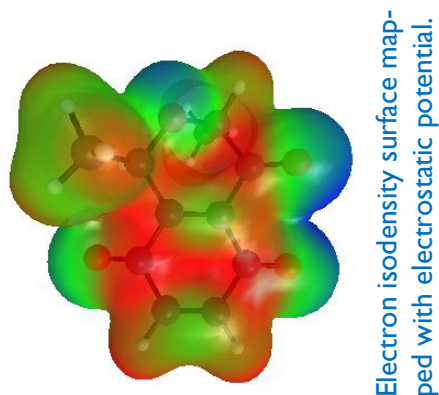
$$\rho(\mathbf{r}) = N \int d\mathbf{r}_2 \int d\mathbf{r}_3 \cdots \int d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$$

Spin density

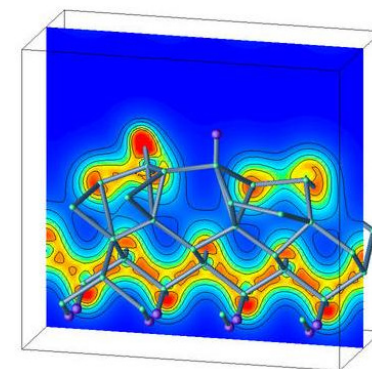
$$\sigma(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$$

Charge density

$$\rho_C(\mathbf{r}) = Ne \int d\mathbf{r}_2 \int d\mathbf{r}_3 \cdots \int d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2$$



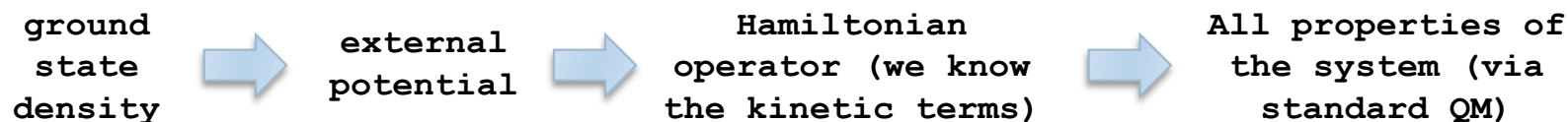
Spin density around an oxygen vacancy in cerium oxide.



Charge density map of a modified silicon surface.

# Density functional theory

The basic lemma of DFT: *the ground state density of a bound system of interacting electrons in some external potential determines this potential uniquely.*



It should therefore be possible to reformulate quantum chemistry in terms of electron density alone (just three dimensions!) – a major simplification.

Hohenberg-Kohn variational principle: *there exists a well-defined (though not explicitly known) functional of electron density, which attains a global minimum at the ground state density.*



Walter Kohn

$$\min_{\rho} E[\rho] = \left\langle \Psi_0 \left| \hat{T} + \hat{V} + \hat{U} \right| \Psi_0 \right\rangle$$

Labels for the equation above:

- $\Psi_0$ : ground state wavefunction
- $\hat{T}$ : kinetic energy
- $\hat{V}$ : nuclear attraction
- $\hat{U}$ : electron repulsion

$$E[\rho] = T[\rho] + U[\rho] + \underbrace{\int V_N(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}}_{\text{nuclear attraction energy functional (known)}}$$

Labels for the equation above:

- $T[\rho]$ : kinetic energy functional (known)
- $U[\rho]$ : inter-electron repulsion energy functional
- $\int V_N(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$ : nuclear attraction energy functional (known)

# Density functional theory

Let us choose a basis and set up a collection of one-electron “orbitals” defined so as to generate some trial density for us to optimize against  $E$ :

$$\text{electron density} \rightarrow \rho(\mathbf{r}) = \sum_{k=1}^N |\chi_k(\mathbf{r})|^2 \quad \chi_k(\mathbf{r}) = \sum_n a_{kn} \varphi_n(\mathbf{r}) \leftarrow \text{basis functions}$$

one-electron “orbitals”

Hartree-Fock style equations for single electrons in these “orbitals” would be:

$$\left[ -\frac{\hbar^2}{2m} \nabla_k^2 + V(\mathbf{r}) \right] \chi_k(\mathbf{r}) = \epsilon_k \chi_k(\mathbf{r})$$

kinetic energy term (known)      potential energy term      energy eigenvalue

The potential is only known partially, all unknowns are dumped into the last term:

$$V(\mathbf{r}) = \sum_n \int \frac{Z_n \rho_1(\mathbf{r}_1)}{|\mathbf{R}_n - \mathbf{r}_2|} d\mathbf{r}_1 + \frac{1}{2} \int \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + V_{\text{XC}} \leftarrow \text{exchange and correlation potential (unknown)}$$

nuclear attraction      inter-electron repulsion

# Exchange-correlation functionals in DFT

The exact form of the exchange-correlation functional is unknown, but several practically usable approximations exist.

**Local spin density approximation (LSDA):** it is assumed that the exchange-correlation energy only depends on the density itself, and not on its derivatives.

$$E_{\text{XC}}^{\text{LDA}}[\rho_{\uparrow}, \rho_{\downarrow}] = \int \rho(\mathbf{r}) \epsilon_{\text{XC}}(\rho_{\uparrow}, \rho_{\downarrow}) d\mathbf{r}$$

↑  
exchange-correlation energy density

**Homogeneous electron gas (HEG):** this is a special case of LSDA. Exchange functional is known exactly and correlation functionals are known in several limits, which are usually interpolated.

**Generalized gradient approximation (GGA):** are local, but also take into account density gradient at each point.

$$E_{\text{XC}}^{\text{GGA}}[\rho_{\uparrow}, \rho_{\downarrow}] = \int \rho(\mathbf{r}) \epsilon_{\text{XC}}(\rho_{\uparrow}, \rho_{\downarrow}, \nabla \rho_{\uparrow}, \nabla \rho_{\downarrow}) d\mathbf{r}$$

**Meta-GGAs** also include second and higher derivatives of the density. This effectively amounts to building more and more accurate Taylor type approximations to the true XC functional.

# Exchange-correlation functionals in DFT

**Hybrid exchange-correlation functional:** a mixture of LDA, GGA and Hartree-Fock exchange (which is known exactly):

$$E_{\text{XC}}^{\text{HYB}} = E_{\text{XC}}^{\text{LDA}} + a_0(E_{\text{X}}^{\text{HF}} - E_{\text{X}}^{\text{LDA}}) + a_{\text{X}}(E_{\text{X}}^{\text{GGA}} - E_{\text{X}}^{\text{LDA}}) + a_{\text{C}}(E_{\text{C}}^{\text{GGA}} - E_{\text{C}}^{\text{LDA}})$$

The coefficients are optimized against experimental data. This disqualifies DFT from the “*ab initio* methods” category – it does require empirical parameters.

TABLE V. Classical reaction barriers (in kcal/mol) computed using BLYP, HCTH, B3LYP, B97 and B97-1 functionals, compared to *ab initio* values.

| Reaction | BLYP  | HCTH  | B3LYP | B97   | B97-1 | <i>Ab initio</i>                      |
|----------|-------|-------|-------|-------|-------|---------------------------------------|
| (I)      | 2.76  | 6.72  | 4.01  | 7.88  | 8.77  | 9.61 <sup>a</sup>                     |
| (II)     | 13.64 | 15.30 | 15.92 | 13.98 | 13.11 | 17.5, <sup>b</sup> 16.60 <sup>c</sup> |
| (III)    | 8.14  | 10.42 | 9.78  | 8.90  | 8.04  | 11.81 <sup>d</sup>                    |
| (IV)     | 3.51  | 6.09  | 6.33  | 5.81  | 5.05  | 9.51 <sup>d</sup>                     |
| (V)      | ...   | 1.32  | 1.23  | 1.31  | 0.67  | 5.62, <sup>d</sup> 4.87 <sup>c</sup>  |
| (VI)     | ...   | 0.94  | 2.58  | 1.90  | 1.30  | 6.62, <sup>e</sup> 5.11 <sup>c</sup>  |

Do not just use B3LYP for everything – check the literature for what works best.

TABLE III. Optimized geometries (in Å and degrees) for selected training set molecules using BLYP, HCTH, B3LYP and B97-1 functionals, compared to reference values.

| Molecule                          | Reference | BLYP  | HCTH  | B3LYP | B97-1 |
|-----------------------------------|-----------|-------|-------|-------|-------|
| H <sub>2</sub>                    | 0.741     | 0.743 | 0.742 | 0.740 | 0.739 |
| LiH                               | 1.596     | 1.598 | 1.616 | 1.589 | 1.596 |
| BeH                               | 1.343     | 1.346 | 1.360 | 1.341 | 1.349 |
| CH                                | 1.120     | 1.133 | 1.133 | 1.123 | 1.127 |
| CH <sub>2</sub> ( <sup>3</sup> B) | 1.078     | 1.083 | 1.081 | 1.077 | 1.080 |
|                                   | 136.0     | 135.7 | 135.2 | 135.3 | 135.1 |
| CH <sub>2</sub> ( <sup>1</sup> A) | 1.110     | 1.119 | 1.119 | 1.110 | 1.113 |
|                                   | 101.9     | 101.9 | 100.6 | 101.8 | 101.4 |
| CH <sub>3</sub>                   | 1.080     | 1.084 | 1.081 | 1.078 | 1.080 |
| CH <sub>4</sub>                   | 1.086     | 1.094 | 1.091 | 1.088 | 1.090 |
| NH                                | 1.036     | 1.051 | 1.045 | 1.041 | 1.042 |
| NH <sub>2</sub>                   | 1.024     | 1.037 | 1.030 | 1.027 | 1.028 |
|                                   | 103.3     | 102.5 | 102.2 | 103.1 | 102.9 |
| NH <sub>3</sub>                   | 1.012     | 1.020 | 1.014 | 1.013 | 1.014 |
|                                   | 106.7     | 106.4 | 105.8 | 106.9 | 106.5 |
| Δ <i>r</i>                        |           | 0.019 | 0.013 | 0.008 | 0.008 |
| Δφ                                |           | 0.4   | 0.7   | 0.2   | 0.3   |

# Exchange-correlation functionals in DFT

TABLE VI. Mean absolute errors (mae) for electron affinities in eV. G2-1 is the original G2 set (25 systems) (Refs. 17,18, and 20). Max ae denotes the maximum absolute error.

|                    | Mae (G2-1) | Max ae(G2-1) |
|--------------------|------------|--------------|
| SVWN <sup>a</sup>  | 0.74       | 1.2          |
| LSD (SVWN5)        | 0.30       | 0.7          |
| PBE                | 0.11       | 0.3          |
| BLYP <sup>a</sup>  | 0.11       | 0.4          |
| B3LYP <sup>a</sup> | 0.11       | 0.5          |
| PBE1PBE            | 0.13       | 0.3          |

TABLE IX. Mean absolute error (mae) in Å for the bond lengths of the diatomics in Table VIII. Max ae denotes the maximum absolute error.

|                    | Mae   | Max ae |
|--------------------|-------|--------|
| LSD (SVWN5)        | 0.016 | 0.095  |
| PBE                | 0.014 | 0.054  |
| BLYP <sup>a</sup>  | 0.019 | 0.045  |
| VSXC <sup>a</sup>  | 0.013 | 0.075  |
| B3LYP <sup>a</sup> | 0.009 | 0.039  |
| PBE1PBE            | 0.009 | 0.055  |

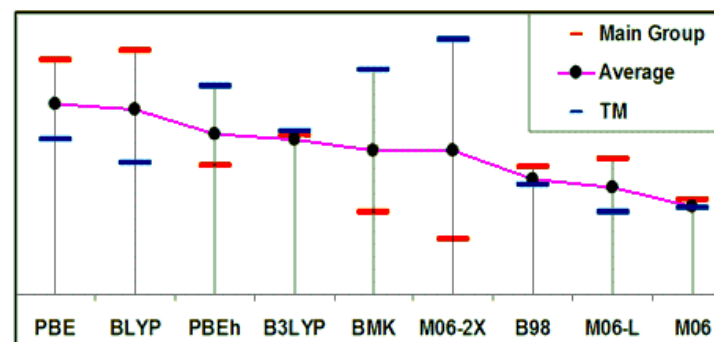
TABLE II. Mean absolute errors (mae) for atomization energies in kcal/mol, obtained from various DFT schemes. G2 denotes the extended G2 set (148 molecules) (Ref. 19) and G2-1 the original G2 set (55 molecules) (Refs. 17 and 18). The maximum absolute errors (max ae) are also listed.

|                    | Mae (G2) | Mae (G2-1) | Max ae (G2) | Max ae (G2-1) |
|--------------------|----------|------------|-------------|---------------|
| SVWN <sup>a</sup>  | 121.2    | 39.6       | 229         | 94            |
| LSD(SVWN5)         | 83.7     | 36.4       | 216         | 84            |
| PBE                | 17.1     | 8.6        | 52          | 26            |
| BLYP <sup>a</sup>  | 7.1      | 4.7        | 28          | 15            |
| VSXC <sup>b</sup>  | 2.7      | 2.5        | 12          | 8             |
| B3LYP <sup>a</sup> | 3.1      | 2.4        | 20          | 10            |
| PBE1PBE            | 4.8      | 3.5        | 24          | 10            |

BLYP and B3LYP are the relatively recent success stories of DFT – Axel Becke’s paper on the subject has collected over 119,000 citations.

TABLE IV. Mean absolute errors (mae) for the ionization potentials (in eV) in the G2-1 set Refs. (17,18 and 20) (the 38 atoms and molecules of Table III). Max ae denotes the maximum absolute error. In some cases self-consistent solutions could not be obtained (see Table III).

|                    | Mae (G2-1) | Max ae(G2-1) |
|--------------------|------------|--------------|
| SVWN               | 0.69       | 1.2          |
| LSD(SVWN5)         | 0.22       | 0.6          |
| PBE                | 0.16       | 0.5          |
| BLYP <sup>a</sup>  | 0.20       | 0.6          |
| VSXC <sup>b</sup>  | 0.13       | 0.4          |
| B3LYP <sup>a</sup> | 0.17       | 0.8          |
| PBE1PBE            | 0.16       | 0.7          |



Of the very recent exchange-correlation functional families, a very promising one is M06.

# Long-range corrected XC functionals

The asymptotic behaviour of the exact exchange potential at long distances matches the Coulomb law ( $-r_{12}^{-1}$ ):

$$E_X^{\text{HF}}[\rho] = \frac{1}{2} \sum_{ij} \iint \frac{\psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \psi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

← density part  
← distance part

However, many DFT exchange functionals do not exhibit this asymptotic behaviour:

$$E_X^{\text{LDA}}[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho(\vec{r})^{4/3} d^3\vec{r}$$

$$E_X^{\text{B88}}[\rho] = E_X^{\text{LDA}}[\rho] - \beta \int \rho^{4/3} \frac{x^2}{1 + \gamma x^2} d^3\vec{r}, \quad x = \frac{|\nabla \rho|}{\rho^{4/3}}$$

$$E_{\text{XC}}^{\text{B3LYP}} = E_{\text{XC}}^{\text{LDA}} + a_0 (E_X^{\text{HF}} - E_X^{\text{LDA}}) + a_X (E_X^{\text{GGA}} - E_X^{\text{LDA}}) + a_C (E_C^{\text{GGA}} - E_C^{\text{LDA}})$$

This is a serious problem – many long-range properties (particularly non-covalent interactions and charge transfer excitations) are not properly reproduced by DFT as a result. Even the generally reliable B3LYP asymptotically behaves as  $-0.2r_{12}^{-1} \dots$

# Long-range corrected XC functionals

An empirical correction may be introduced by blending the short-range DFT exchange with long-range Hartree-Fock exchange. Ewald split is commonly used:

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}, \quad \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

Multiplying the two terms by different functionals creates a smooth transition between approximations. A generalization, known as *Coulomb-attenuating method* (CAM) appears to be particularly successful:

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \text{erf}(\mu r_{12})}{r_{12}}$$

