Density Functional Theory (DFT)

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Outline

The electron density and early models based on the density

Hohenberg–Kohn Theorems and the Bright Wilson observation

Kohn–Sham theory

Practical aspects of KS calculations, including numerical quadrature

Excited states

Integer discontinuity and self-interaction

The local density approximation (LDA) and scaling relationships

Generalised gradient approximations (GGAs) and meta GGAs

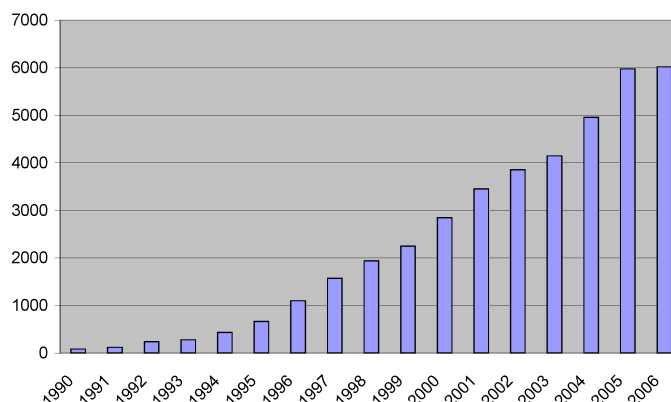The adiabatic connection—hybrid functionals (eg B3LYP!)

Coulomb attenuated functionals

Are we really doing Kohn–Sham theory? The optimised effective potential (OEP)

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Introductory Comments

Enormous growth in DFT calculations since the early 1990s. Why?

Correlated methods based on the wavefunction scale poorly with system size and need large basis sets to describe electron–electron cusp. Cannot apply to large molecules.

DFT is based on the electron density, which is a very simple quantity (3 variables compared to $3N$). DFT is therefore a simple theory. Many similarities to Hartree–Fock but DFT is formally *exact*.

In practice, have to make approximations. Standard DFT approximations scale like Hartree–Fock. Furthermore, basis set must describe the density, not the wavefunction. Hence less need for high angular momentum functions. Result: DFT allows good quality correlated calculations at low cost; can be applied to very large systems.

The electron density

The quantity $|\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 d\mathbf{x_1} d\mathbf{x_2} \ldots d\mathbf{x_N}$ is the probability of finding electron 1 in $d\mathbf{x_1}$, electron 2 in $d\mathbf{x_2}$, etc. Integrating over the space-spin coordinates of electrons $2, 3, \ldots, N$, together with the spin coordinate of electron 1, gives

$$\left(\int \cdots \int |\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 ds_1 d\mathbf{x_2} \cdots d\mathbf{x}_N \right) d\mathbf{r_1} , \tag{1}$$

which is the probability of finding electron 1 in volume element $d\mathbf{r_1}$, whilst the other electrons are anywhere. Multiplying by N gives the probability of finding any electron in $d\mathbf{r_1}$,
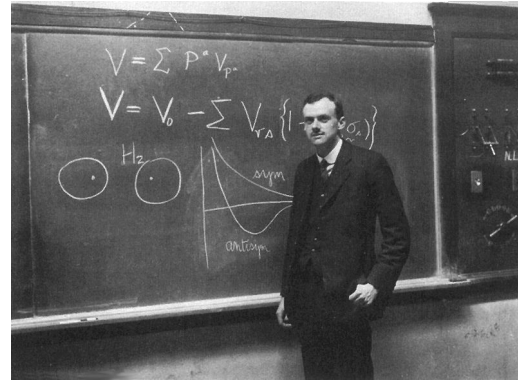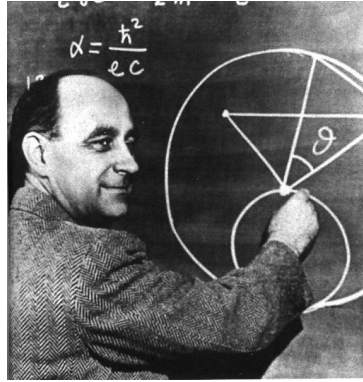
$$\left(N \int \cdots \int |\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 ds_1 d\mathbf{x_2} \cdots d\mathbf{x}_N \right) d\mathbf{r_1} = \rho(\mathbf{r_1}) d\mathbf{r_1} , \tag{2}$$

The quantity $\rho(\mathbf{r_1})$ is the electron density

$$\rho(\mathbf{r_1}) = N \int \cdots \int |\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots \mathbf{x_N})|^2 ds_1 d\mathbf{x_2} \cdots d\mathbf{x}_N \tag{3}$$

Early models based on the density (1920s)

The electron–nuclear attraction and classical electron–electron repulsion energies can be written exactly in terms of the density (see later).

Thomas, Fermi, Dirac, and others attempted to also express the kinetic and exchange energies in terms of the density

$$T[\rho] \;=\; C_{\mathrm{T}} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \tag{4}$$

$$E_{\mathrm{X}}[\rho] \;=\; C_{\mathrm{X}} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \tag{5}$$

Little quantitative use due to errors in $T[\rho]$.

At that time, there was no rigorous proof that the electronic energy could be expressed in term of the density (ie as a _functional_ of the density).

Rigorous Proof: The Hohenberg–Kohn Theorems
Phys. Rev. **136** B864 (1964)

The electronic Hamiltonian is

$$\hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{V}_{\text{ee}} = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_i^N v(\mathbf{r}_i) + \sum_{i<j}^N \frac{1}{r_{ij}} \tag{6}$$

where the external potential is

$$v(\mathbf{r}_i) = -\sum_A \frac{Z_A}{r_{Ai}} \tag{7}$$

Theorem 1: 'The electron density determines the external potential'

Proof:

$$\hat{H} = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_i^N v(\mathbf{r}_i) + \sum_{i<j}^N \frac{1}{r_{ij}} \qquad (8)$$

Let there be two external potentials $v_1(\mathbf{r})$ and $v_2(\mathbf{r})$ arising from the same density $\rho(\mathbf{r})$. There will be two Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ with the same ground state density, but different wavefunctions Ψ_1 and Ψ_2. From the variational principle

$$E_1^0 < \langle\Psi_2|\hat{H}_1|\Psi_2\rangle = \langle\Psi_2|\hat{H}_2|\Psi_2\rangle + \langle\Psi_2|\hat{H}_1 - \hat{H}_2|\Psi_2\rangle \qquad (9)$$
$$= E_2^0 + \int \rho(\mathbf{r})[v_1(\mathbf{r}) - v_2(\mathbf{r})]d\mathbf{r} \qquad (10)$$

The subscripts 1 and 2 can be interchanged to give a second inequality. Adding the two gives

$$E_1^0 + E_2^0 < E_2^0 + E_1^0 \qquad (11)$$

which is a contradiction.

Hence, external potential is uniquely determined (to within trivial constant) by $\rho(\mathbf{r})$.

The density also trivially determines the number of electrons N

$$\int \rho(\mathbf{r})d\mathbf{r} = N \tag{12}$$

Now look back at the Hamiltonian

$$\hat{H} = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_i^N v(\mathbf{r}_i) + \sum_{i<j}^N \frac{1}{r_{ij}} \tag{13}$$

The density $\rho(\mathbf{r})$ determines both $v(\mathbf{r}_i)$ AND the number of electrons N.

Hence the density determines the Hamiltonian $\hat{H}$.

Hence the density determines the wavefunction Ψ and everything about the system!

Hence can develop a theory that uses the electron density as the fundamental variable.

$\rightarrow$ Density Functional Theory (DFT)

The Bright Wilson observation

To know the Hamiltonian, we need to know the number of electrons and the external potential, ie the number of electrons, the nuclear charges, and their positions. All of these can be determined from a knowledge of the density:

$$\int \rho(\mathbf{r})d\mathbf{r} = N \qquad \frac{\partial}{\partial r_A}\overline{\rho}(r_A)\big|_{r_A=0} = -2Z_A\overline{\rho}(0) \qquad (14)$$

where $\overline{\rho}$ is the spherical average of the density. The cusps of the density tell us where the nuclei are.

$\rho(\mathbf{r})$ therefore determines the Hamiltonian and hence everything about the system.

We therefore write the electronic energy as a *functional* of the density

$$E[\rho] = V_{\mathrm{ne}}[\rho] + T[\rho] + V_{\mathrm{ee}}[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[\rho] \qquad (15)$$

where $T[\rho]$ is the kinetic energy, $V_{ee}[\rho]$ is the electron–electron interaction energy, and $F[\rho]$ is a universal functional of ρ

$$F[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] = \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi \rangle \qquad (16)$$

The second Hohenberg–Kohn theorem allows us to introduce a variational principle. Any approximate density $\tilde{\rho}$ determines $\tilde{v}$ and hence its own wavefunction $\tilde{\Psi}$. Using this wavefunction in the usual variational principle gives

$$\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle = \int \tilde{\rho}(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[\tilde{\rho}] = E[\tilde{\rho}] \geq E[\rho] \qquad (17)$$

We therefore need to minimise the energy with respect to density variations, subject to the constraint $\int \rho(\mathbf{r})d\mathbf{r} = N$.

To minimise a *function* $E(x)$ wrt x, subject to a constraint $G(x) = c$, we set

$$\frac{\partial}{\partial x}\left(E(x) - \mu\left[G(x) - c\right]\right) = 0 \qquad \frac{\partial E(x)}{\partial x} - \mu\frac{\partial G(x)}{\partial x} = 0 \qquad (18)$$

where $\frac{\partial E(x)}{\partial x}$ is defined by

$$E(x + \delta x) - E(x) = \delta x\frac{\partial E(x)}{\partial x} + \dots \qquad (19)$$

To minimise a *functional* $E[\rho]$ wrt $\rho(\mathbf{r})$, subject to a constraint $G[\rho] = c$, we set

$$\frac{\delta}{\delta\rho(\mathbf{r})}\left(E[\rho] - \mu\left[G[\rho] - c\right]\right) = 0 \qquad \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} - \mu\frac{\delta G[\rho]}{\delta\rho(\mathbf{r})} = 0 \qquad (20)$$

where $\frac{\delta E[\rho]}{\partial\rho(\mathbf{r})}$ is the <u>functional derivative</u>, defined by

$$E[\rho + \delta\rho] - E[\rho] = \int \frac{\delta E[\rho]}{\delta\rho(\mathbf{r})}\, \delta\rho(\mathbf{r})d\mathbf{r} + \dots \qquad (21)$$

Often encounter functionals of the form $E[\rho] = \int F(\rho, \nabla\rho)d\mathbf{r}$ for which

$$\frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} = \frac{\partial F}{\partial\rho} - \nabla \cdot \frac{\partial F}{\partial\nabla\rho} \qquad (22)$$

See Appendix in book for more details.

So for our DFT minimisation with constraint $\int \rho(\mathbf{r})d\mathbf{r} = N$, we have

$$\frac{\delta}{\delta\rho(\mathbf{r})} \left(E[\rho] - \mu \left[\int \rho(\mathbf{r})d\mathbf{r} - N \right] \right) = 0 \tag{23}$$

$$\frac{\delta E[\rho]}{\delta\rho(\mathbf{r})} - \mu = 0 \tag{24}$$

Finally, given that

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[\rho] \tag{25}$$

we have

$$\mu = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} \tag{26}$$

Eqn. (26) is the Euler–Lagrange equation, which can be solved for the exact density

The Levy Constrained Search Formulation (1979)

The original Hohenberg–Kohn analysis involved a minimisation over all v-representable densities (ie those associated with an antisymmetric ground state wavefunction of a Hamiltonian of the form $H = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_i^N v(\mathbf{r}_i) + \sum_{i<j}^N \frac{1}{r_{ij}})$. Conditions for v-representable density are not known! Problem!

Alternative view:

$$
\begin{aligned}
E_0 &= \min_{\Psi}\langle\Psi|\hat{T} + \hat{V}_{\text{ee}} + \sum_i^N v(\mathbf{r}_i)|\Psi\rangle \\
&= \min_{\rho}\left(\min_{\Psi\to\rho}\langle\Psi|\hat{T} + \hat{V}_{\text{ee}} + \sum_i^N v(\mathbf{r}_i)|\Psi\rangle\right) \\
&= \min_{\rho}\left(\min_{\Psi\to\rho}\langle\Psi|\hat{T} + \hat{V}_{\text{ee}}|\Psi\rangle + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\right) \\
&= \min_{\rho}\left(F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}\right) \qquad (27)
\end{aligned}
$$

Fully consistent with earlier, but demonstrates that we only need to consider N-representable densities (ie those associated with an antisymmetric N-electron wavefunction Ψ). v-representability problem eliminated; easier.

So we have equation for the exact $\rho(\mathbf{r})$ ...

$$
\begin{aligned}
\mu &= v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \\
&= v(\mathbf{r}) + \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\mathrm{ee}}[\rho]}{\delta \rho(\mathbf{r})}
\end{aligned}
\tag{28}
$$

Problem: In practice, we need to approximate $T[\rho]$ and $V_{\mathrm{ee}}[\rho]$. The former is very large (Virial theorem!), so even small errors in this term can make the theory useless (recall Thomas–Fermi).

Solution ...

Kohn–Sham Theory

Introduce orbitals into the problem, such that the kinetic energy can be computed to good accuracy, leaving a small residual correction.

The Kohn–Sham analysis is as follows . . .

Recall that the electronic energy can be written exactly as

$$E[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F[\rho] \tag{29}$$

Kohn and Sham defined

$$F[\rho] = T_{\mathrm{s}}[\rho] + J[\rho] + E_{\mathrm{XC}}[\rho] \tag{30}$$

where J is the classical Hartree (Coulomb) repulsion of the density

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 \tag{31}$$

and $T_s[\rho]$ is the kinetic energy of a system of non-interacting electrons with density ρ. Given that

$$F[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] \tag{32}$$

it follows that the the *exchange–correlation energy* is

$$E_{\mathrm{XC}}[\rho] = T[\rho] - T_{\mathrm{s}}[\rho] + V_{\mathrm{ee}}[\rho] - J[\rho] \tag{33}$$

Minimising the Kohn–Sham energy expression

$$E = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + T_{\mathrm{s}}[\rho] + J[\rho] + E_{\mathrm{XC}}[\rho] \qquad (34)$$

with respect to the density (subject to fixed N) gives the Euler equation

$$\mu = v_{\mathrm{eff}}(\mathbf{r}) + \frac{\delta T_{\mathrm{s}}[\rho]}{\delta \rho(\mathbf{r})} \qquad (35)$$

where

$$v_{\mathrm{eff}} = v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta \rho(\mathbf{r})} \qquad (36)$$

Eqn. (35)—which yields the exact density of the system—is just the conventional DFT Euler equation

$$\mu = v(\mathbf{r}) + \frac{\delta T[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\mathrm{ee}}[\rho]}{\delta \rho(\mathbf{r})} \qquad (37)$$

for a system of non-interacting electrons $(T = T_s;\ V_{\mathrm{ee}} = 0)$ moving in an external potential $v_{\mathrm{eff}}(\mathbf{r})$. Hence the density of the real (interacting) system is exactly the same as the density of a non-interacting system with external potential $v_{\mathrm{eff}}(\mathbf{r})$.
We can calculate this!!

The Hamiltonian for a system of non-interacting electrons moving in an external potential $v_{\text{eff}}(\mathbf{r})$ is

$$\hat{H} = -\sum_i^N \frac{1}{2}\nabla_i^2 + \sum_i^N v_{\text{eff}}(\mathbf{r}_i) \tag{38}$$

This is separable—the exact wavefunction is just a single determinant constructed from orbitals that are the solutions to

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \tag{39}$$

The density and kinetic energy of this non-interacting system are just

$$\rho(\mathbf{r}) = \sum_i^N \varphi_i^2(\mathbf{r}) \qquad T_{\text{s}}[\rho] = \sum_i^N \langle\varphi_i| -\frac{1}{2}\nabla^2|\varphi_i\rangle \tag{40}$$

Summary: Solve Eqns (39) (the 'Kohn–Sham equations') using $v_{\text{eff}} = v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\text{XC}}[\rho]}{\delta\rho(\mathbf{r})}$ and evaluate $\rho(\mathbf{r})$ and $T_{\text{s}}[\rho]$ using Eqn. (40). Then evaluate the total energy of the real system as $E = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + T_{\text{s}}[\rho] + J[\rho] + E_{\text{XC}}[\rho]$.

An exact theory! Nobel Prize, 1998

Majority of $T[\rho]$ now described exactly; just need to approximate smaller $E_{\text{XC}}[\rho]$.

The equations of Kohn–Sham (KS) theory

$$E = \sum_i^N \langle \varphi_i | -\frac{1}{2}\nabla^2 |\varphi_i\rangle + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + J[\rho] + E_{\mathrm{XC}}[\rho] \qquad (41)$$

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta\rho(\mathbf{r})}\right)\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \qquad (42)$$

bear a striking resemblance to those of Hartree–Fock (HF) theory

$$E = \sum_i^N \langle \varphi_i | -\frac{1}{2}\nabla^2 |\varphi_i\rangle + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + J[\rho] + E_{\mathrm{X}}^0 \qquad (43)$$

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})}\right)\varphi_i(\mathbf{r}) + \int X(\mathbf{r}, \mathbf{r}')\varphi_i(\mathbf{r}')d\mathbf{r}' = \epsilon_i\varphi_i(\mathbf{r}) \qquad (44)$$

To go from HF (no correlation) to KS (correlated), replace the HF exchange energy and *non-multiplicative* exchange operator with the exchange–correlation energy and *multiplicative* exchange–correlation potential

$$v_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta\rho(\mathbf{r})} \qquad (45)$$

As with Hartree–Fock theory, expand the molecular orbitals in a Gaussian (or other) basis set to form the matrix secular equations.

Only difference is that the X contribution to the Fock matrix is replaced by an XC contribution

$$\int \eta_\alpha \, v_{\text{XC}} \, \eta_\beta \, d\mathbf{r} \tag{46}$$

Solve SCF equations as in Hartree–Fock (DIIS, etc).

Should use unrestricted for open-shells, in order to allow negative spin densities. Programs will indicate 'spin contamination', meaning $\langle S^2 \rangle \neq S(S+1)$. However, this refers to the non-interacing system, not the physical system.

Chemistry is much more than just the electronic energy—also need to calculate molecular properties. To do so, replace the X terms of HF theory with the XC terms of KS theory.

Numerical Quadrature

We have seen that new integrals arise in DFT. They cannot be evaluated analytically due to fractional powers of the density. Must use numerical quadrature. Consider the general molecular integral

$$\int F(\mathbf{r})d\mathbf{r} \qquad eg \ \ F = \rho^{4/3} \tag{47}$$

First, following Becke (JCP **88** 2547), we decompose the integrand into components localised on the nuclei. To do this, we define atomic weights $w_A(\mathbf{r})$, which are near unity near nucleus A, but zero near all other nuclei, and which satisfy $\sum_A w_A(\mathbf{r}) = 1$. Inserting this into Eqn. (47) gives

$$\int F(\mathbf{r})d\mathbf{r} = \int \left(\sum_A w_A(\mathbf{r}) \right) F(\mathbf{r})d\mathbf{r} = \sum_A \int w_A(\mathbf{r})F(\mathbf{r})d\mathbf{r} = \sum_A \int F_A(\mathbf{r})d\mathbf{r}$$

where $F_A(\mathbf{r})$ is a function localised around nucleus A. Each localised integral is then evaluated using standard r, θ, ϕ numerical integration, centered on that nucleus

$$\int F_A(\mathbf{r})d\mathbf{r} \approx \sum_i F_A(\mathbf{r}_i)w_i \tag{48}$$

HK theorems use the variational principle. Hence can only apply DFT to lowest state of any space-spin symmetry. Excitation energies determined from these energies are termed 'delta SCF' excitations. Limited applicability. Rigorous approach is to use time-dependent DFT (TDDFT).

Vertical excitation energies ω are determined from

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \tag{49}$$

which can be derived either from a density-matrix linear-response approach or from the poles of the dynamic polarisability. In practical calculations, the dimension of the problem can then be reduced by one half by exploiting the fact that the matrix $(\mathbf{A} - \mathbf{B})$ is positive definite for real orbitals, leading to the alternative expression

$$(\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2}\mathbf{Z} = \omega^2 \mathbf{Z} \tag{50}$$

where

$$\mathbf{Z} = (\mathbf{A} - \mathbf{B})^{-1/2}(\mathbf{X} + \mathbf{Y}) \tag{51}$$

provides information about which occupied orbital rotates into which virtual orbital, allowing the excitation energies to be assigned. The precise form of the matrices $\mathbf{A}$ and $\mathbf{B}$ depends on the nature of the exchange–correlation functional (see later). For hybrid functionals, for example, which combine a GGA functional with a fraction ξ of exactly computed exchange, they are

$$
\begin{aligned}
A_{ia,jb} &= \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|jb) - \xi(ij|ab) + (1 - \xi)(ia|f_{\mathrm{XC}}|jb) \\
B_{ia,jb} &= (ia|bj) - \xi(ij|aj) + (1 - \xi)(ia|f_{\mathrm{XC}}|jb)
\end{aligned} \tag{52}
$$

where

$$(ia|f_{\mathrm{XC}}|jb) = \int d\mathbf{r}d\mathbf{r}' \varphi_i(\mathbf{r})\varphi_a(\mathbf{r}) \frac{\delta^2 E_{\mathrm{XC}}^{\mathrm{GGA}}}{\delta\rho(\mathbf{r})\rho(\mathbf{r}')} \varphi_b(\mathbf{r})\varphi_j(\mathbf{r}) \tag{53}$$

Note that we have used the usual adiabatic approximation, which assumes that the density varies slowly in time; the time-dependent exchange–correlation potential is replaced by the conventional (time-independent) potential, evaluated using the time-dependent density.

Integer discontinuity and self-interaction

Thorough understanding—particularly for excited states—requires an understanding of *fractional* numbers of electrons!

1.Exact E vs N curve is series of straight lines (PRL **49** 1691) with slopes

$$\left.\frac{\partial E}{\partial N}\right|_{N-f} = -I \qquad \left.\frac{\partial E}{\partial N}\right|_{N+f} = -A \tag{54}$$

A functional satisfying this is said to be many-electron self-interaction free.

Implication: Exact $v_{\mathrm{XC}}(\mathbf{r})$ jumps discontinuously by an amount $\triangle_{\mathrm{XC}}$ (several eV!) as N crosses the integer and the exact Kohn–Sham orbital energies satisfy

$$\epsilon_{\mathrm{HOMO}}^{-} = -I \qquad \epsilon_{\mathrm{LUMO}}^{+} = -A \tag{55}$$

2. For $0 \leq N \leq 1$, no two-electron energy, hence $E_{\mathrm{XC}}[\rho] = -J[\rho]$. A functional satisfying this is said to be 1-electron self-interaction free.

The exchange–correlation energy

Fundamental problem: don't know how to write down the exchange–correlation energy $E_{\text{XC}}[\rho]$. Common approximations include (<u>omitting spin labels for clarity</u>):

Local density approximation (LDA)

$$E_{\text{XC}} = \int F(\rho)d\mathbf{r} \tag{56}$$

Generalised gradient approximation (GGA)

$$E_{\text{XC}} = \int F(\rho, \nabla\rho)d\mathbf{r} \tag{57}$$

Meta GGAs

$$E_{\text{XC}} = \int F(\rho, \nabla\rho, \nabla^2\rho)d\mathbf{r} \tag{58}$$

Hybrids

$$E_{\text{XC}} = \int F(\rho, \nabla\rho)d\mathbf{r} + \xi E_{\text{X}}^0 \tag{59}$$

Jacob's Ladder! We now consider all these (and others) in turn . . .

The local density approximation (LDA, 1965)

Start with a model where exact results can be derived: the uniform electron gas. This is an infinite system of constant electron density (balanced by a positive background).

The exchange energy is defined by (recall Hartree–Fock)

$$E_{\mathrm{X}} = -\frac{1}{4} \iint \frac{|\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \tag{60}$$

where ρ_1 is the 1-particle density matrix

$$\rho_1(\mathbf{r}_1, \mathbf{r}_2) = 2 \sum_i \varphi_i(\mathbf{r}_1)\varphi_i(\mathbf{r}_2) \tag{61}$$

Evaluating the exchange energy using the KS orbitals for a uniform gas

$$\varphi(k_x, k_y, k_z) = \frac{1}{V^{1/2}} \exp(i\mathbf{k}.\mathbf{r}) \tag{62}$$

gives (after some maths—see book)

$$E_{\mathrm{X}} = C_{\mathrm{X}} \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \qquad C_{\mathrm{X}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \qquad [\text{Dirac}] \tag{63}$$

A similar analysis for the kinetic energy gives

$$T = C_{\mathrm{F}} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \qquad C_{\mathrm{F}} = \frac{3}{10} \left(3\pi^2\right)^{2/3} \quad [\mathrm{Thomas - Fermi}] \qquad (64)$$

Ceperley and Alder used quantum Monte-Carlo to simulate the uniform electron gas and hence determined the correlation energy. This was put into a functional form by Vosko, Wilk, and Nusair (VWN) and later updated by Perdew and Wang (PW). Again, it is a functional of just the density.

In the LDA, the exchange and correlation components of E_{XC} are approximated using the Dirac and VWN/PW expressions, i.e. we apply locally a result that is valid for a uniform gas of electrons.

The LDA can be surprising successful in some cases (eg molecular structures), but there is one very serious problem—it significantly overbinds molecules. It is therefore of limited use in Chemistry, although it is still widely used in Physics. Why?!

Scaling Relationships

The form of the LDA exchange and kinetic energies can be derived very simply from scaling conditions. A knowledge of these conditions will also help us understand more advanced exchange approximations ...

Define a scaled electron density and scaled 1-particle density matrix

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r}) \qquad \rho_{1\lambda}(\mathbf{r}_1, \mathbf{r}_2) = \lambda^3 \rho_1(\lambda \mathbf{r}_1, \lambda \mathbf{r}_2) \tag{65}$$

where the λ^3 ensures that the scaled density still integrates to N electrons. Evaluation of the exact (HF) exchange energy using the latter gives

$$
\begin{aligned}
E_{\mathrm{X}}^0[\rho_\lambda] &= \int \frac{|\rho_{1\lambda}(\mathbf{r}_1, \mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 = \lambda^6 \int \frac{|\rho_1(\lambda \mathbf{r}_1, \lambda \mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\
&= \lambda^6 \int \frac{|\rho_1(\mathbf{r}'_1, \mathbf{r}'_2)|^2}{\lambda^{-1} r'_{12}} \frac{d\mathbf{r}'_1}{\lambda^3} \frac{d\mathbf{r}'_2}{\lambda^3} = \lambda E_{\mathrm{X}}^0[\rho]
\end{aligned}
\tag{66}
$$

which can be viewed as an exact exchange condition.

If we now assume that the DFT exchange energy takes the form

$$E_{\mathrm{X}}[\rho] = \int \rho^n(\mathbf{r})d\mathbf{r} \tag{67}$$

then

$$E_{\mathrm{X}}[\rho_\lambda] = \int \rho_\lambda^n(\mathbf{r})d\mathbf{r} = \lambda^{3n}\int \rho^n(\lambda\mathbf{r})d\mathbf{r} = \lambda^{3n}\int \rho^n(\mathbf{r}')\frac{d\mathbf{r}'}{\lambda^3} = \lambda^{3n-3}E_{\mathrm{X}}[\rho] \tag{68}$$

Hence, to satisfy the scaling condition, we must have

$$3n - 3 = 1 \tag{69}$$
$$n = 4/3 \tag{70}$$

which is exactly the Dirac form!

A similar analysis for the kinetic energy gives

$$T[\rho_\lambda] = \lambda^2 T[\rho] \tag{71}$$

The increased power of λ explains why the kinetic term has $5/3$ rather than $4/3$.

Generalised gradient approximations (GGA, 1980s)

Problem with LDA—assumes constant electron density. Not true! Natural next step is to introduce information about the density gradient $\rightarrow$ GGAs.

$x(\mathbf{r}) = \frac{\nabla \rho(\mathbf{r})}{\rho^{4/3}(\mathbf{r})}$ is dimensionless, meaning that it does not introduce any powers of λ when $\rho \rightarrow \rho_\lambda$. Correct exchange scaling can therefore be achieved from the form

$$E_X[\rho] = \int \rho^{4/3}(\mathbf{r}) f(x(\mathbf{r})) d\mathbf{r} \qquad (72)$$

A natural choice is the gradient expansion $f = C_X + \gamma x^2$, but the XC potential diverges. The famous Becke 1988 (B88X) functional uses $f = C_X + \beta x^2/(1 + 6\beta x \sinh^{-1} x)$, in order to ensure correct long-range behaviour of the energy density and a non-divergent potential. Parameter β <u>fitted</u> to atomic exchange energies.

Also in 1988, Lee, Yang and Parr (LYP) and Miehlich *et al* derived a correlation functional from the Colle–Salvetti formula for the He atom, again depending on ρ and $\nabla \rho$.

The combination of B88X + LYP = BLYP was responsible for the acceptance of DFT by quantum chemists. See book for further details.

Note that for GGA functionals,

$$E_{\text{XC}}[\rho] = \int F(\rho, \nabla\rho) d\mathbf{r} \tag{73}$$

the XC contribution to the Kohn–Sham (Fock) matrix is

$$\int \eta_\alpha \, v_{\text{XC}} \, \eta_\beta \, d\mathbf{r} = \int \eta_\alpha \left(\frac{\partial F}{\partial \rho} - \nabla \cdot \frac{\partial F}{\partial \nabla\rho} \right) \eta_\beta \, d\mathbf{r} \tag{74}$$

which requires the second derivative of F. In practical calculations, we avoid this by evaluating the mathematically equivalent (integration by parts)

$$\int \eta_\alpha \, v_{\text{XC}} \, \eta_\beta \, d\mathbf{r} = \int \eta_\alpha \, \frac{\partial F}{\partial \rho} \, \eta_\beta \, d\mathbf{r} + \int \frac{\partial F}{\partial \nabla\rho} \cdot \nabla(\eta_\alpha \eta_\beta) \, d\mathbf{r} \tag{75}$$

Many other GGAs in the literature! Two approaches
1. Derived from theoretical arguments, eg PW91,PBE
2. Derived from a semi-empirical fit, eg (BLYP), OLYP, HCTH

Why do GGAs work?

$$V_{ee}[\rho] = J[\rho] + \frac{1}{2}\iint \frac{\rho(\mathbf{r}_1)\rho_{XC}(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 \tag{76}$$

where $\rho_{XC}(\mathbf{r}_1,\mathbf{r}_2)$ is the *exchange–correlation hole* of an electron at $\mathbf{r}_1$. This is a unit charge with sign opposite to that of the electron, which represents a reduction in probability around each electron. Consider stretched H_2. The exact *exchange* hole is $-\rho(\mathbf{r})/2$, and so it is delocalised over both centres. By contrast, the exact *exchange–correlation* hole for an electron near one nucleus is *localised* around that nucleus, in order to ensure that $V_{ee} = 0$. The difference between the two holes represents left–right electron correlation.

By contrast, the GGA exchange hole is *localised* and so it recovers both exchange and left–right correlation. This is clear from the energy: GGA exchange energies are very close to exact exchange energies for atoms, but they are notably lower for molecules, reflecting left–right correlation. GGA correlation functionals just model dynamic correlation and so adding a GGA exchange to a GGA correlation functional yields a complete picture of exchange, left–right correlation, and dynamic correlation. Simply adding GGA correlation to exact exchange misses left–right correlation!

Typical GGA performance for selected properties

Mean absolute errors:

	PBE	HCTH
Atomisation Energies (kcal/mol)	16.5	5.5
Bond Lengths (Å)	0.015	0.013
Reaction Barriers (kcal/mol)	7.8	3.8
NMR Shieldings (ppm)	40	32
Local Excitations (eV)	0.2	0.2
Rydberg Excitations (eV)	> 1	> 1
Charge Transfer Excitations (eV)	> 1	> 1

Notes

Atomisation energies and other energy quantities such as IPs, EAs, PAs, are quite reasonable. Bond lengths also reasonable.

Barriers underestimated. Often attributed to fact that GGAs are not self-interaction free.

NMR shieldings significantly underestimated. For GGAs, magnetic hessian matrix is diagonal (equations collapse because the density remains real in the presence of a magnetic field) and the paramagnetic shielding is explicitly dependent on the reciprocal of occupied–virtual orbital energy differences. GGAs tend to underestimate this quantity, hence shieldings are too paramagnetic, ie too low. Can be fixed with specially designed functionals (JCP **121** 5654), which increase energy differences.

Local excitations are quite reasonable. Rydbergs and CT can both be significantly underestimated! Why is this?

Exchange–correlation potentials from GGAs

To understand why local excitations are OK, but Rydberg and CT are so poor, we must consider how GGAs handle the integer discontinuity.

In regions where density is significant, GGA potentials approximately average over the discontinuity, giving HOMO and LUMO orbitals energies of

$$\epsilon_{\text{HOMO}} \approx -I + \frac{\Delta_{\text{XC}}}{2} \qquad \epsilon_{\text{LUMO}} \approx= -A - \frac{\Delta_{\text{XC}}}{2} \tag{77}$$

Given that the *shape* of the potential is reasonably accurate in this regions, it follows that low lying excitations are reasonable.

At larger distances, however, the potential collapses to zero, rather than approaching the appropriate value of $\frac{\Delta_{\text{XC}}}{2}$. Hence Rydberg excitations are much too low. Can be fixed by grafting on the correct behaviour, which is

$$\lim_{r \to \infty} v_{\text{XC}}(\mathbf{r}) = -1/r + \frac{\Delta_{\text{XC}}}{2} = -1/r + \epsilon_{\text{HOMO}} + I \tag{78}$$

See JCP **109** 10180

To understand the charge-transfer error, consider an excitation that transfers an electron from a donor (D) to an acceptor (A), which are infinitely separated. The exact excitation energy is just

$$\omega^{\text{exact}} = I^{\text{D}} - A^{\text{A}} \tag{79}$$

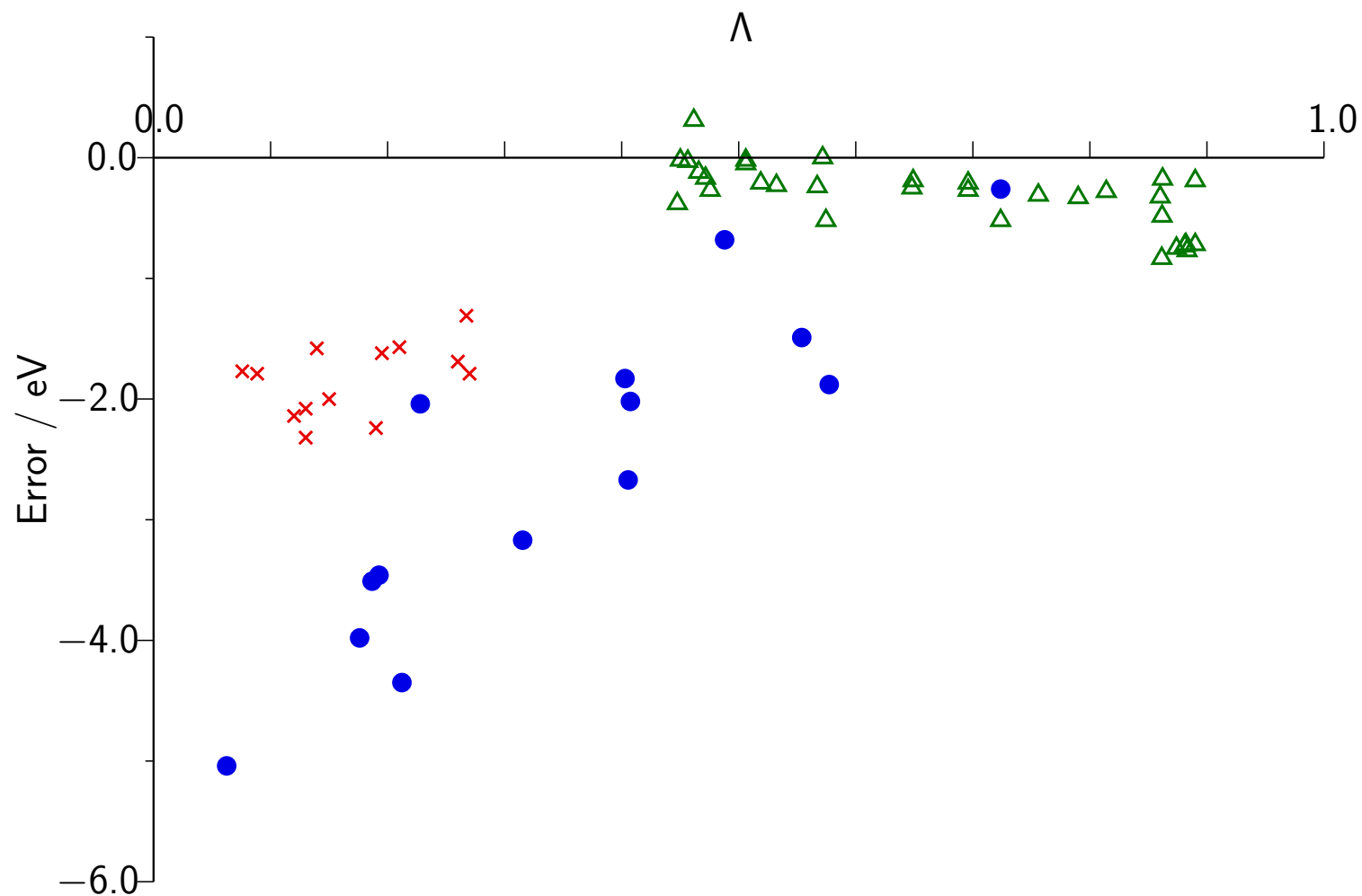Due to the lack of overlap between D and A, the GGA excitation is just

$$
\begin{aligned}
\omega^{\text{GGA}} = \epsilon^{\text{A}}_{\text{LUMO}} - \epsilon^{\text{D}}_{\text{HOMO}} &= I^{\text{D}} - A^{\text{A}} - \frac{1}{2}\left(\Delta^{\text{D}}_{\text{XC}} + \Delta^{\text{A}}_{\text{XC}}\right) \\
&= \omega^{\text{exact}} - \frac{1}{2}\left(\Delta^{\text{D}}_{\text{XC}} + \Delta^{\text{A}}_{\text{XC}}\right) \tag{80}
\end{aligned}
$$

Hence, GGAs approximately underestimate by the average of the integer discontinuities! Several eV!
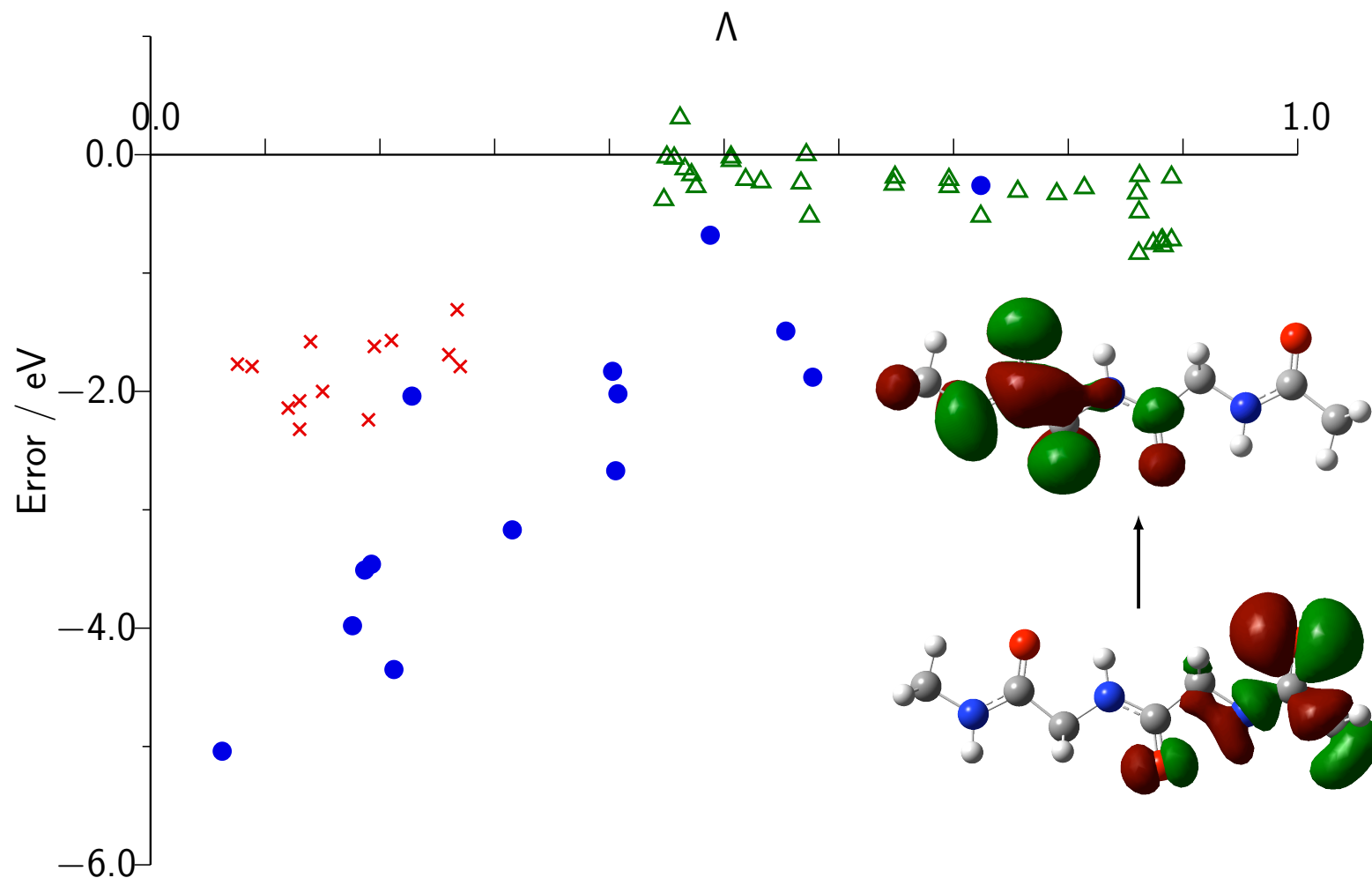
See JCP **119** 12697

Correlation between error and orbital overlap?

JCP **128** 044118 (2008)
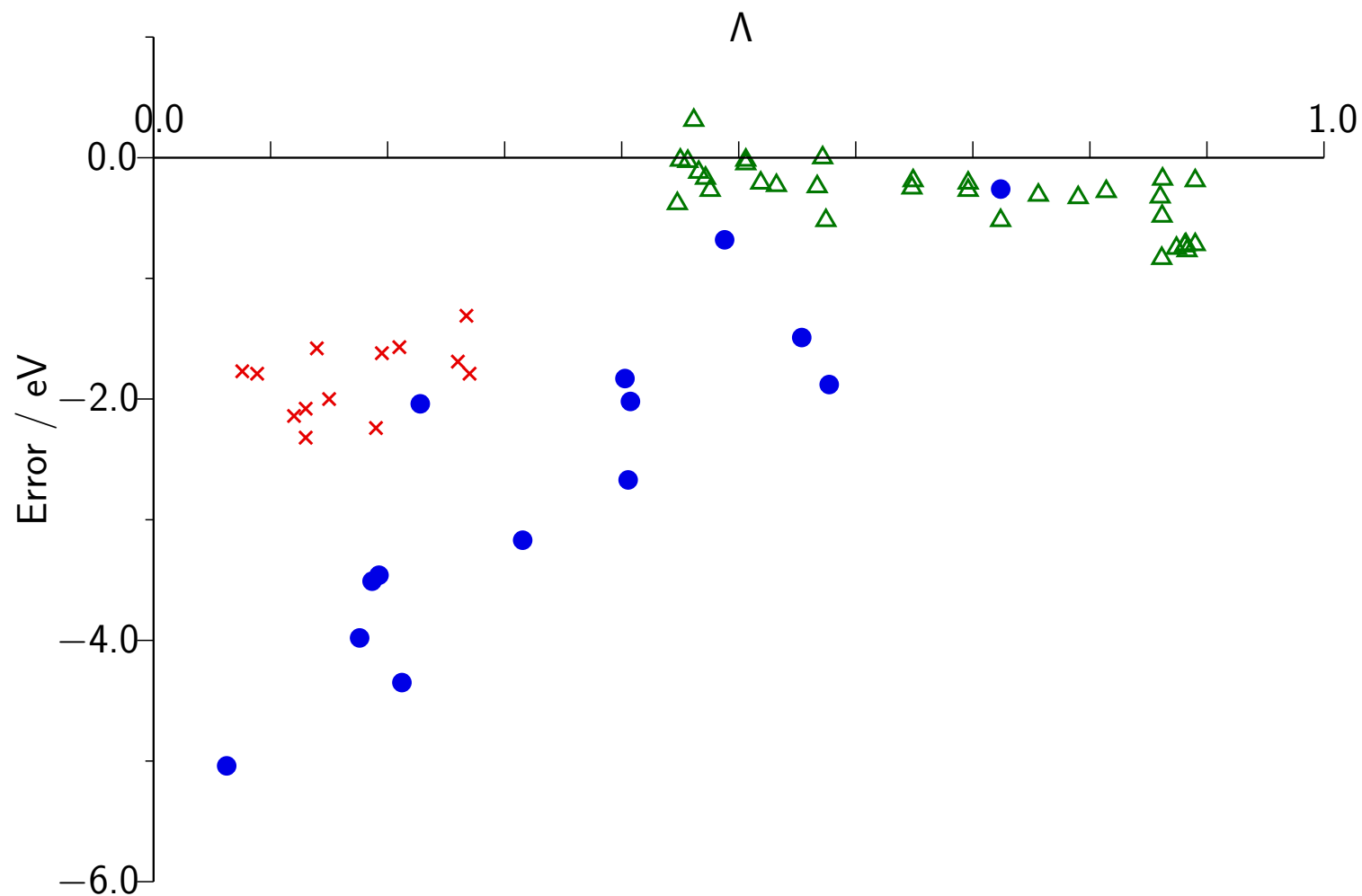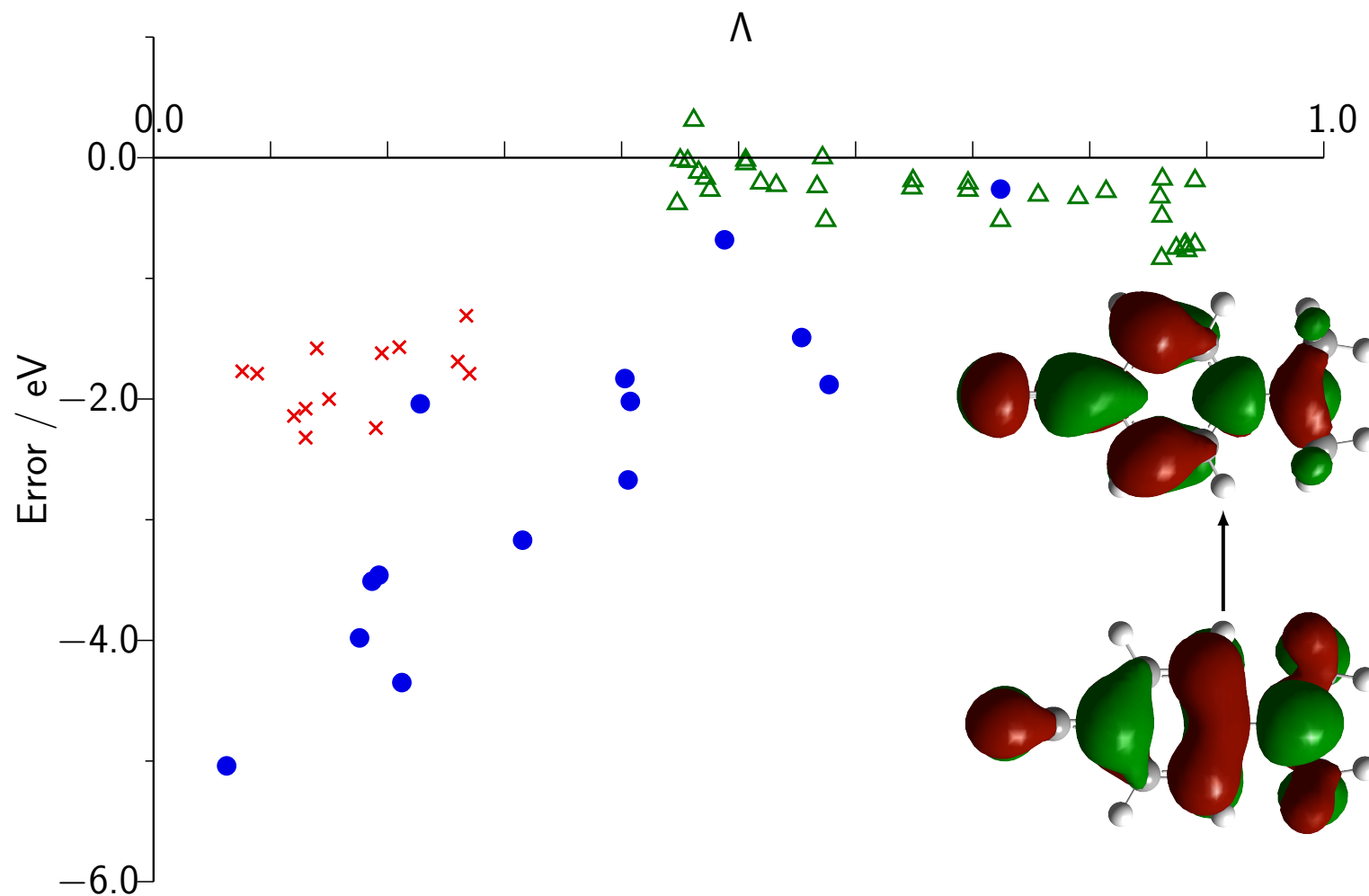
JCP **131** 091101 (2009)

Correlation between error and orbital overlap?

Correlation between error and orbital overlap?

JCP **128** 044118 (2008)

JCP **131** 091101 (2009)

Correlation between error and orbital overlap?

Λ

0.0   1.0

Error / eV

JCP **128** 044118 (2008)

JCP **131** 091101 (2009)

37

Meta GGAs

The natural next step is to introduce higher derivatives into the functional, namely the density Laplacian, $\nabla^2 \rho$ and the kinetic energy density, $\tau = \sum_i |\nabla \varphi_i|^2$

Examples include VSXC, PKZB, TPSS

Not very widely used in chemistry. No major improvments. Further research needed.

The adiabatic connection → Hybrid functionals (1990s)

Recall the definition of $F[\rho]$ from the constrained search analysis

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi \rangle \tag{81}$$

Generalise to

$$F_\lambda[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{\mathrm{ee}} | \Psi \rangle = \langle \Psi_\lambda | \hat{T} + \lambda \hat{V}_{\mathrm{ee}} | \Psi_\lambda \rangle \tag{82}$$

where Ψ_λ is the wavefunction that minimises $\langle \hat{T} + \lambda \hat{V}_{\mathrm{ee}} \rangle$, whilst giving the exact density. We have

$$F_1[\rho] = T[\rho] + V_{\mathrm{ee}}[\rho] \qquad F_0[\rho] = T_{\mathrm{s}}[\rho] \tag{83}$$

Hence

$$E_{\mathrm{XC}}[\rho] = T[\rho] - T_{\mathrm{s}}[\rho] + V_{\mathrm{ee}}[\rho] - J[\rho] = F_1[\rho] - F_0[\rho] - J[\rho] \tag{84}$$

and so

$$E_{\mathrm{XC}}[\rho] = \int_0^1 \frac{\partial F_\lambda[\rho]}{\partial \lambda} d\lambda - J[\rho] = \int_0^1 \langle \Psi_\lambda | \hat{V}_{\mathrm{ee}} | \Psi_\lambda \rangle \, d\lambda - J[\rho] \tag{85}$$

We write this as

$$E_{\text{XC}}[\rho] = \int\limits_0^1 W_\lambda d\lambda \tag{86}$$

where

$$W_\lambda = \langle \Psi_\lambda | \hat{V}_{\text{ee}} | \Psi_\lambda \rangle - J[\rho] \tag{87}$$

Becke (JCP **98** 1372) tried $W_\lambda = a + b\lambda$, determining a and b from $\lambda = 0, 1$

$$W_0 = a = E_{\text{X}}^0 \qquad W_1 = a + b = V_{\text{ee}} - J \approx U_{\text{XC}}^{\text{LDA}} \tag{88}$$

The resulting energy is then

$$E_{\text{XC}}[\rho] = a + \frac{b}{2} = \frac{1}{2}E_{\text{X}}^0 + \frac{1}{2}U_{\text{XC}}^{\text{LDA}} \tag{89}$$

This is the 'Half and Half functional', which is very successful for certain properties.

The key observation is that E_{XC} must include exact exchange, E_{X}^0!

Functionals containing some exact exchange are termed 'hybrid' functionals.

By introducing semi-empirical parameters, Becke determined the B3P91 functional

$$\text{B3P91} \equiv (1 - A)E_X^{\text{Dirac}} + AE_X^0 + B\Delta E_X^{\text{Becke88}}$$
$$+ E_C^{\text{VWN}} + CE_C^{\text{Perdew91}} \tag{90}$$

with optimum parameters $A = 0.20$, $B = 0.72$, $C = 0.81$.

A minor modification led to the ubiquitous B3LYP functional (JCP **98** 5648)

$$\text{B3LYP} \equiv (1 - A)E_X^{\text{Dirac}} + AE_X^0 + B\Delta E_X^{\text{Becke88}}$$
$$+ (1 - C)E_C^{\text{VWN}} + CE_C^{\text{LYP}} \tag{91}$$

B3LYP has had an enormous impact in chemistry!

Citations in Each Year
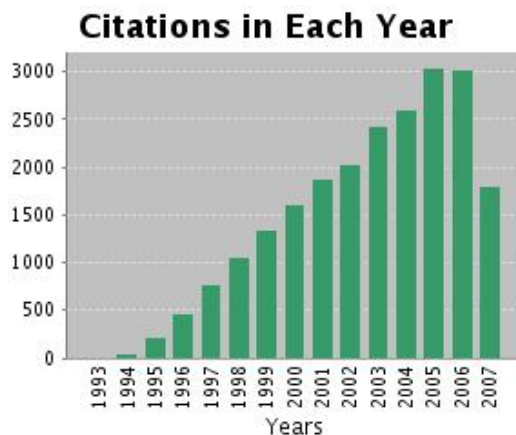
Kohn–Sham equations for hybrid functionals

Hybrid functionals take the general form

$$E_{\text{XC}} = \int F(\rho, \nabla\rho)d\mathbf{r} + \xi E_{\text{X}}^0 \qquad (92)$$

Electronic structure programs (Gaussian, Dalton, Cadpac, Gamess, etc, etc) solve the following Kohn–Sham equation for the KS orbitals and orbital energies

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\text{XC}}^{\text{GGA}}[\rho]}{\delta\rho(\mathbf{r})}\right)\varphi_i + \xi \int X(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')d\mathbf{r}' = \epsilon_i\varphi_i \quad (93)$$

which is a mixture of KS and HF approaches!

This is not strictly KS theory! See later for the proper solution!

Other hybrids in the literature! Two approaches
1. Derived from theoretical arguments, eg PBE0
2. Derived from a semi-empirical fit, eg B97-2

Typical hybrid performance, compared to HCTH GGA

Mean absolute errors:

	HCTH	B3LYP	B97-2
Atomisation Energies (kcal/mol)	5.5	4.2	3.1
Bond Lengths (Å)	0.013	0.008	0.008
Reaction Barriers (kcal/mol)	3.8	5.1	2.4
NMR Shieldings (ppm)	32	61	50
Local Excitations (eV)	0.2	0.2	0.2
Rydberg Excitations (eV)	> 1	> 0.8	> 0.8
Charge Transfer Excitations (eV)	> 1	> 0.8	> 0.8

Notes

Atomisation energies and other energy quantities such as IPs, EAs, PAs, together with bond lengths, are an improvement over GGA. Generally very good.

Barriers improved, but still underestimated. Still not self-interaction free. Specialist functionals have been designed to improve barriers(eg MPW1K).

NMR shieldings less accurate than GGA! Very unusual to find this! More difficult to calculate too as magnetic hessian matrix not diagonal as usually implemented. Can be traced to comment regarding the nature of the orbital equations. See later!

Local excitations are quite reasonable. Rydbergs and CT improve slightly, but can still be in significant error (just 20% exact exchange).

Recent adiabatic connection work

Mori-Sánchez *et al.* recently considered the alternative adiabatic connection

$$W_\lambda = a + \frac{b\lambda}{1 + c\lambda} \tag{94}$$

They set a to be the exact exchange energy; b to be an approximate initial slope; and c to reproduce an approximate W_λ value from BLYP.

The key feature is that for one electron systems, $b = 0$ and so the exchange–correlation energy reduces to the exchange energy, which exactly cancels the coulomb energy. Hence the functional is one-electron self-interaction free.

The functional is not, however, many electron self-interaction free.

Improved reaction barriers, but otherwise rather like B3LYP.

Coulomb attenuated functionals (2000s)

Hybrid functionals ($\xi = 0.20 - 0.25$) do a good job of describing short range electron-electron interactions, as demonstrated by the fact that short-range properties such as atomisation energies, bond lengths, are well described.

However, these functionals provide a poor description of long-range interactions, as demonstrated by the fact that long-range properties such as Rydberg and charge-transfer excitation energies are poor.

To fix the long-range problem, we need more exact exchange

However, simply increasing the amount of exact exchange in a conventional hybrid functional is not helpful, as short range properties will degrade!

One solution to this problem is *Coulomb Attenuation*, where the amount of exact exchange increases as the interaction becomes more long-ranged

Initial idea—Tsuneda *et al.*

$$\frac{1}{r_{12}} \equiv \frac{\text{erf}(\mu r_{12})}{r_{12}} + \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} = \text{LR} + \text{SR} \qquad (95)$$

First component gives LR exchange, evaluated using modified exact orbital expression

Second component gives SR exchange, evaluated using modified GGA

The amount of exchange increases from 0 to 100% as r_{12} increases, i.e. behaves like GGA at short range. Hence not as good as a hybrid for atomisation energies, etc.

Solution—Yanai *et al.*

$$\frac{1}{r_{12}} \equiv \frac{[\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} + \frac{1 - [\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} \qquad (96)$$

This alternative partitioning gives a functional with α exact exchange at short range and $\alpha + \beta$ at long-range. By having $\alpha \approx 0.2$, will maintain hybrid quality short range properties. But having $\beta > 0$ will also lead to improved long-range properties.

$$E_{\mathrm{X}}^{\mathrm{LR}} = \alpha E_{\mathrm{X}}^{0} - \frac{\beta}{2} \sum_{\sigma} \sum_{ij} \iint \psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)\frac{\mathrm{erf}(\mu r_{12})}{r_{12}}\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{\mathrm{X}}^{\mathrm{SR}} = -\frac{1}{2} \sum_{\sigma} \int \rho_{\sigma}^{4/3} K_{\sigma}^{\mathrm{GGA}} \left\{ (1-\alpha) - \beta \left(\frac{8}{3} a_{\sigma} \left[\sqrt{\pi}\mathrm{erf}\left(\frac{1}{2a_{\sigma}}\right) + 2a_{\sigma}(b_{\sigma}-c_{\sigma}) \right] \right) \right\} d\mathbf{r}$$

$$E_{\mathrm{XC}}^{\mathrm{CAM\text{-}B3LYP}} = E_{\mathrm{X}}^{\mathrm{LR}} + E_{\mathrm{X}}^{\mathrm{SR}}[\mathrm{Becke88}] + E_{\mathrm{C}}^{\mathrm{B3LYP}} \tag{97}$$

$$E_{\mathrm{C}}^{\mathrm{B3LYP}} = 0.81 \ E_{\mathrm{C}}^{\mathrm{LYP}} + 0.19 \ E_{\mathrm{C}}^{\mathrm{VWN}} \tag{98}$$

$\mu = 0.33 \ au$, $\alpha = 0.19$, $\beta = 0.46$ defines the CAM-B3LYP functional.

See CPL **393** 51 (2004)

Typical CAM-B3LYP performance, compared to B3LYP

	B3LYP	CAM-B3LYP
Atomisation Energies (kcal/mol)	4.2	3.9
Bond Lengths (Å)	0.008	0.009
Reaction Barriers (kcal/mol)	5.1	3.6
NMR Shieldings (ppm)	61	60
Local Excitations (eV)	0.2	0.2
Rydberg Excitations (eV)	> 0.8	> 0.3
Charge Transfer Excitations (eV)	> 0.8	> 0.3

CAM-B3LYP (and related funtionals) have a much smaller many-electron self-interaction error (ie closer to linearity in E vs N plot).

The optimised effective potential (OEP)

As noted earlier, in standard implementations (Gaussian, Dalton, etc), the KS equations for hybrid functionals take the form

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\mathrm{XC}}^{\mathrm{GGA}}[\rho]}{\delta\rho(\mathbf{r})} \right) \varphi_i + \xi \int X(\mathbf{r},\mathbf{r}')\varphi_i(\mathbf{r}')d\mathbf{r}' = \epsilon_i\varphi_i \quad (99)$$

This is obtained by minimising the energy with respect to the _orbitals_ (like in HF).

This is not KS theory. KS theory requires us to minimise with respect to the _density_, to give an equation of the form

$$\left(-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{\mathrm{XC}}^{\mathrm{Hybrid}}[\rho]}{\delta\rho(\mathbf{r})} \right) \varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \quad (100)$$

This is difficult, because hybrid functionals are functionals of both the density and the orbitals. The rigorous solution to this problem is the Optimised Effective Potential (OEP).

Do the maths and find you have to solve the following integral equation

$$\sum_i \int d\mathbf{r}' [v_{\mathrm{XC}}(\mathbf{r}') - u_{\mathrm{XC}i}(\mathbf{r}')] G(\mathbf{r}', \mathbf{r}) \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}') = 0 \qquad (101)$$

where

$$u_{\mathrm{XC}i}(\mathbf{r}) = \frac{1}{\varphi_i(\mathbf{r})} \frac{\delta E_{\mathrm{XC}}^{\mathrm{Hybrid}}}{\delta \varphi_i(\mathbf{r})} \qquad G(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}')}{\epsilon_i - \epsilon_j} \qquad (102)$$

A challenge! Approximations have been suggested, KLI, LHF, CEDA.

Conceptually and computationally simpler approach: Write the potential in the KS equation as the sum of a known part plus a linear combination of gaussian functions. Then evaluate the derivative of the energy with respect to the expansion coefficients and do a direct minimisation. See Wu and Yang, PRL **89** 143002 (2002).

Thermochemistry and structures barely affected in going from conventional to OEP. But, magnetic response parameters are <u>enormously</u> affected. Errors typically reduced by factor of 3–4 in shielding constants, magnetisabilities, and rotational g tensors (J. Chem. Theory Comput. **2** 827)

Summary and remaining challenges

GGA functionals were the first widely used approximations in chemistry, 1980s; significant improvement over LDA in describing bond breaking.

Superseded by hybrid functionals in the 1990s; significantly improved thermochemistry and structures but still problems with long range properties

Coulomb attenuated approximations can maintain the good short-range performance of hybrids, but improve long-range; better description of E vs N curve.

Magnetic response parameters poor from all the above, when determined in the conventional (non-KS) manner; dramatic improvements when evaluated using OEP.

Present status encouraging, but many challenges remain:

- Further systematic improvement of E_{XC}. Balance of exact and approximate X.

- Improved correlation functionals, particularly with regard to near-degeneracy effects and dispersion interactions. The former is necessary for molecular dissociation, eg to dissociate H_2 requires a divergence in the slope of W_λ. The latter is completely absent from conventional local functionals; non-locality is essential. Non-local forms do exist but are not widely used at present. More commonly, the long-range R^{-6} is simply added to conventional DFT approximations.

- Improved description of the integer discontinuity and MESIE.

- Robust schemes for calculating OEP potentials; the Wu–Yang scheme needs two basis sets (orbitals and potential) and if they are not balanced then unphysical potentials are obtained.

- Introduction of explicit current-dependence into functionals. Magnetic props?

- Moving beyond the adiabatic approximation in TDDFT; memory effects.

- Moving beyond the density; two-particle information; calculation of $\langle \hat{S}^2 \rangle$.

- Orbital free DFT; representation of T_s as an explicit, rather than implicit, functional of the density.