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REGULAR ARTICLE

The importance of Colle–Salvetti for computational density functional theory

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Abstract The purpose of this presentation is to show the importance of the Colle–Salvetti (Theor Chim Acta 37:329, 1975) paper in the development of modern computational density functional theory. To do this we cover the following topics (1) the Bright Wilson understanding (2) the Kohn–Sham equations (3) local density exchange (4) the exchange-hole (5) generalised gradient approximation for exchange (Becke and Cohen) (6) left–right correlation and dynamic correlation (7) the development of the Lee–Yang–Parr dynamic correlation functional from the Colle–Salvetti paper (8) the early success of GGA DFT. Finally we observe that the the BLYP and OLYP exchange-correlation functionals are not semi-empirical; this may explain their great success.

1 Introduction

The purpose of this paper is to show why the original paper of Colle and Salvetti was so important in the development of computational density functional theory for chemistry. To do this it is necessary to proceed through the historical development and understanding of exchange and correlation. Much of the paper is therefore a reproduction of earlier work, but taken as a whole, I hope it makes a convincing story!

2 The Bright Wilson understanding

Professor Robert G Parr told me that when Walter Kohn presented his first paper [1] on density functional theory (DFT) at a conference in 1965, the eminent spectroscopist Bright Wilson made the following comments

(1) $\int \rho(\mathbf{r})d\mathbf{r} = n$, where $\rho(\mathbf{r})$ is the electron density and n is the number of electrons.
(2) The density is cusped at all nuclei, and only cusped at nuclei.
(3) The shape of the cusp determines the specific nucleus.

Thus the Schrodinger Hamiltonian H is known, and from $H\Psi = E\Psi$, the energy is known, and therefore $E = E[\rho]$.

This is a very simple understanding of the theory behind DFT for chemistry.

3 The Kohn–Sham equations

It is well established that a functional representation for the kinetic energy with good accuracy is impossible to find, but that $\langle\phi| -\frac{1}{2}\nabla^2\phi\rangle$ is the quantum mechanical representation for the kinetic energy of orbital ϕ.

Therefore Kohn and Sham [2] proposed

$$\rho(\mathbf{r}) = \sum_i^n \phi_i^2(\mathbf{r}) \tag{1}$$

We can write

$$E[\rho] = T_s[\rho] + V_{\mathrm{ne}}[\rho] + J[\rho] + E_{\mathrm{xc}}[\rho] \tag{2}$$

where $T_s[\rho]$ is the Laplacian representation of the kinetic energy, V_{ne} is the nuclear attraction energy, J is the Coulomb energy and E_{xc} is the remainder, which certainly

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includes exchange and correlation. By representing the orbitals in terms of a basis set

$$\phi_i(\mathbf{r}) = \sum_{\alpha}^{m} d_{\alpha i}\eta_\alpha(\mathbf{r}). \tag{3}$$

we can minimise the energy with respect to the molecular orbital coefficients to give the Kohn–Sham equations

$$\begin{aligned}\langle\eta_\beta(\mathbf{r})| &-\frac{1}{2}\nabla^2 + v_{\mathrm{ne}}(\mathbf{r}) + v_J(\mathbf{r}) + v_{\mathrm{xc}}(\mathbf{r}) \\ &- \epsilon_i|\sum_{\alpha} d_{\alpha i}\eta_\alpha(\mathbf{r})\rangle = 0.\end{aligned} \tag{4}$$

Here v_{ne} is the nuclear attraction potential, v_J is the coulomb potential (both known) and v_{xc} is the unknown exchange correlation potential.

The problem is therefore to find a good expression for $E_{\mathrm{xc}}[\rho]$. The KS equations are fundamental to modern DFT.

4 Local density exchange

Before we can discuss electron correlation, we must have exchange completely understood. For the uniform electron gas, Dirac [3] obtained an exact expression for the exchange energy $E_x[\rho]$

$$E_x = -\frac{1}{2}\sum_{ij}^{\sigma}(ij|ij) = -C_X\sum_{\sigma}\int \rho_\sigma^{4/3}(\mathbf{r})\mathrm{d}\mathbf{r} = E_x[\rho] \tag{5}$$

where $C_X = \frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3}$, and σ denotes the spins α, β. This term must be the dominant part of E_{xc}. The Dirac term is now denoted LDAX.

5 The exchange-hole

This is an important aspect in the understanding of DFT.

The exchange expression may be written as

$$E_x = -\frac{1}{2}\sum_{\sigma}\iint \rho_\sigma(\mathbf{r_1})\frac{1}{r_{12}}\rho_{x\sigma}(\mathbf{r_1},\mathbf{r_2})\mathrm{d}\mathbf{r_1}\mathrm{d}\mathbf{r_2} \tag{6}$$

where

$$\rho_{x\sigma}(\mathbf{r_1},\mathbf{r_2}) = \sum_{ij}^{\sigma}\frac{\phi_{i\sigma}(\mathbf{r_1})\phi_{j\sigma}(\mathbf{r_1})\phi_{i\sigma}(\mathbf{r_2})\phi_{j\sigma}(\mathbf{r_2})}{\rho_\sigma(\mathbf{r_1})} \tag{7}$$

from which it follows that

$$\int \rho_{x\sigma}(\mathbf{r_1},\mathbf{r_2})\mathrm{d}\mathbf{r_2} = 1 \tag{8}$$

We say that the exchange-hole, surrounding $\mathbf{r_1}$, contains one electron.

For a one determinant representation for H_2, $\mathcal{A}(\sigma_g^2)$ we have $\rho_{\mathrm{xc}}(\mathbf{r_1},\mathbf{r_2}) = \sigma_g^2(\mathbf{r_2})$. Thus the exchange-hole has 0.5 electron near proton A and 0.5 electron near proton B, for all $\mathbf{r_1}$, for all R. This is clearly wrong; if the reference electron is near A, then the exchange-hole should be near A.

When R is very large, the exact wavefunction is $\frac{1}{2^{1/2}}(\mathcal{A}(\sigma_g^2) - \mathcal{A}(\sigma_u^2))$, with $\rho = \sigma_g^2 + \sigma_u^2 = 2\rho_\sigma$. Because there is no dynamic correlation, $E_x[\rho] = E_{\mathrm{exact}} - J[\rho]$, from which it can be deduced that

$$\rho_{x\sigma}(\mathbf{r_1},\mathbf{r_2}) = \frac{\sigma_g(\mathbf{r_1})\sigma_u(\mathbf{r_1})\sigma_g(\mathbf{r_2})\sigma_u(\mathbf{r_2}) + \sigma_g^2(\mathbf{r_1})\sigma_u^2(\mathbf{r_2})}{\rho_\sigma(\mathbf{r_1})}. \tag{9}$$

It may then be shown that

(1) if $\mathbf{r_1}$ is near A and $\mathbf{r_2}$ is near B, then $\rho_{\mathrm{xc}}(\mathbf{r_1},\mathbf{r_2}) = 0$, i.e. no exchange-hole near B,
(2) if $\mathbf{r_1}$ and $\mathbf{r_2}$ are both near A, then $\rho_{\mathrm{xc}}(\mathbf{r_1},\mathbf{r_2}) = 1$, i.e. the exchange-hole is near A.

From which we deduce that CI has introduced ‘left–right’ correlation through the exchange term.

If we introduce the ‘spherically averaged’ exchange-hole

$$\rho_{x\sigma}(\mathbf{r_1},s) = \frac{1}{4\pi}\int \rho_{x\sigma}(\mathbf{r_1},\mathbf{r_1}+\mathbf{s})\mathrm{d}\Omega_s \tag{10}$$

then from Dirac’s work, it may be shown for the uniform electron gas that

$$\rho_{x\sigma}(\mathbf{r_1},s) = 9\rho_\sigma\frac{j_1^2(k_{F\sigma}s)}{(k_{F\sigma}s)^2} \tag{11}$$

where $j_1(x)$ is the first order spherical Bessel function and $k_{F\sigma} = (6\pi^2\rho_\sigma)^{1/3}$. The exchange-hole is therefore localised near the reference electron, for all positions of the reference electron. Since all exchange functionals include a very large percentage of LDAX, this argument holds for all exchange functionals.

In summary DFT exchange functionals introduce ‘left–right’ correlation.

6 The generalised gradient approximation for exchange (Becke and Cohen)

For molecular systems, the density is confined and it is not uniform. We cannot expect LDAX to be adequate.

In atoms, there is no left–right correlation; there is only one centre; the only correlation is dynamic. We must expect therefore that DFT calculations with good exchange functionals should give energies very close to Hartree–Fock. We therefore empirically determine generalised gradient exchange functionals which do this:

1. Becke (1988) B88X [4]

   $$E_x[\rho] = -\sum_\sigma C_X \int \rho_\sigma^{4/3} \mathrm{d}\mathbf{r} - \sum_\sigma \int \frac{\beta \rho_\sigma^{4/3} x_\sigma^2}{(1 + 6\beta x_\sigma \sinh^{-1} x_\sigma)} \mathrm{d}\mathbf{r} \tag{12}$$

   with $\beta = 0.0042$, $x = |\nabla \rho| \rho^{-4/3}$. This functional was determined to give best agreement with the HF energies of He, Ne, Ar, Kr and Xe.
2. Handy and Cohen (2002) OPTX [5]

   $$E_x[\rho] = -\sum_\sigma \int (1.05151 C_X + 1.43169 u_\sigma^2) \rho_\sigma^{4/3} \mathrm{d}\mathbf{r} \tag{13}$$

   where $u = \gamma x^2/(1 + \gamma x^2)$, with $\gamma = 0.006$. Determined to give best agreement with HF energies of H–Ar.

For the 18 atoms H–Ar, the mean absolute difference between KS energies for LDAX, B88X, OPTX, and HF are 674.5, 7.40 and 3.56 kcal mol^{-1}. Becke's exchange functional improved predictions by two orders of magnitude!

7 Left–right and dynamic correlation

We have argued that atoms only have dynamic correlation; there is no left–right correlation because there is only one nuclear centre. Likewise H_2 at infinite nuclear separation only has left–right correlation; there is no dynamic correlation because the electrons are never close together. Dynamic correlation is all about electrons avoiding each other when close together; this arises because of the r_{12}^{-1} replusion. He only has dynamic correlation, and this is the start of Colle and Salvetti's work.

The uniform electron gas has dynamic electron correlation. In a famous paper, Ceperley and Alder [6] determined its value numerically through Quantum Monte Carlo simulation (100 electrons in a box, of variable dimension to give different densities). Vosko, Wilk and Nusair (VWN, [7]) then determined a functional $E_c[\rho] = E_c(\rho)$ for this correlation. At first one may think that B88X + VWN = BVWN would be a good exchange-correlation functional, but it is not. VWN is the correlation functional for an infinite system, electrons can avoid one another by going far far apart, whereas molecules are finite systems. There is too much correlation in VWN. Thus it is far better to develop a correlation functional which is based on an atom, like He.

8 The development of the Lee–Yang–Parr correlation functional from the Colle–Salvetti paper

The key papers for the development of the dynamic correlation functional, now known as Lee, Yang and Parr (LYP), are (a) Colle and Salvetti (CS) [8], (b) LYP [9], (c) Miehlich, Savin, Stoll and Preuss (MSSP) [10]. Pople was the first to perform computational DFT using the combinations of exchange and correlation functionals outlined in this paper [11].

(a) Now we will go through the CS paper, with added comments.

1. CS start from an attractive wavefunction

   $$\Psi(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_N}) = \Psi_{\mathrm{HF}}(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_N}) \times \Pi_{i>j}(1 - \phi(\mathbf{r_i}, \mathbf{r_j})) \tag{14}$$

   $$= \Psi_{\mathrm{HF}} \Pi_{i>j}\left(1 - \exp(-\beta^2 r^2)\left(1 - \Phi(\mathbf{R})\left(1 + \frac{r}{2}\right)\right)\right) \tag{15}$$

   where $r = |\mathbf{r_i} - \mathbf{r_j}|$, $\mathbf{R} = \frac{1}{2}(\mathbf{r_i} + \mathbf{r_j})$. Note that the electron–electron cusp condition is forced (which may not be optimum). This is a classic Jastrow wavefunction. The value of the Jastrow function at electron coalescence is $\Phi(\mathbf{r})$.
2. They argue that the volume of the correlation hole ($\pi^{3/2}\beta^{-3}$) should be proportional to Wigner's [12] exclusion volume ($k\rho^{-1}$), and thus $\beta = q\rho^{1/3}$, which is clear on dimension grounds.
3. The 2-particle density matrix is well given in terms of its HF analogue and correlation corrections

   $$P_2(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r}'_1, \mathbf{r}'_2) = P_{2\mathrm{HF}}(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r}'_1, \mathbf{r}'_2)(1 - \phi(\mathbf{r_1}, \mathbf{r_2}) - \phi(\mathbf{r}'_1, \mathbf{r}'_2) + \phi(\mathbf{r_1}, \mathbf{r_2})\phi(\mathbf{r}'_1, \mathbf{r}'_2)) \tag{16}$$

   and most reasonably, to maintain the HF electronic distribution, the 1-particle density matrix is the HF form

   $$P_1(\mathbf{r_1}; \mathbf{r}'_1) = P_{1\mathrm{HF}}(\mathbf{r_1}; \mathbf{r}'_1) \tag{17}$$
4. The correlation energy is then given in terms of the diagonal HF 2-particle density matrix by

   $$E_c = \frac{1}{2} \iint P_{2\mathrm{HF}}(\mathbf{r_1}, \mathbf{r_2})(\phi^2(\mathbf{r_1}, \mathbf{r_2}) - 2\phi(\mathbf{r_1}, \mathbf{r_2})) \frac{1}{r} \mathrm{d}\mathbf{r_1} \mathrm{d}\mathbf{r_2} \tag{18}$$

   This is the expression which CS simplify. The 1-particle matrix condition (17) yields

   $$\int P_{2\mathrm{HF}}(\mathbf{r_1}, \mathbf{r_2}; \mathbf{r}'_1, \mathbf{r_2})(\phi(\mathbf{r_1}, \mathbf{r_2})\phi(\mathbf{r}'_1, \mathbf{r_2}) - \phi(\mathbf{r_1}, \mathbf{r_2}) - \phi(\mathbf{r}'_1, \mathbf{r_2})) \mathrm{d}\mathbf{r_2} = 0 \tag{19}$$
5. This condition is then used to obtain an equation for $\Phi(\mathbf{r})$ by removing $\Phi(\mathbf{r})$ and $P_{2\mathrm{HF}}(\mathbf{r_1}, \mathbf{r_2})$ from under the integral, on the grounds that $\exp(-\beta^2 r^2)$ rapidly decreases to zero with increasing r. Considerable algebra is needed to obtain the equation, which is well satisfied by

$$\Phi(\mathbf{r}) = \frac{\pi^{1/2}\beta}{1+\pi^{1/2}\beta} \tag{20}$$

We interpret this equation for $\Phi(\mathbf{r})$ as one which governs the extent of the correlation hole, dependent on $\rho(\mathbf{r})$ through β.

6. The correlation energy expression (18) is rewritten

$$E_c = -\frac{1}{2}\int P_{2\mathrm{HF}}(\mathbf{R},\mathbf{R})\Biggl(\int \frac{P_{2\mathrm{HF}}(\mathbf{R}+\frac{\mathbf{r}}{2};\mathbf{R}-\frac{\mathbf{r}}{2})}{P_{2\mathrm{HF}}(\mathbf{R},\mathbf{R})} \times\Bigl(2\exp(-\beta^2r^2)\Bigl(1-\Phi(\mathbf{R})\Bigl(1+\frac{r}{2}\Bigr)\Bigr) - \exp(-2\beta^2r^2)\Bigl(1-\Phi(\mathbf{R})\Bigl(1+\frac{r}{2}\Bigr)\Bigr)^2\Bigr)\frac{\mathrm{d}\mathbf{r}}{r}\Biggr)\mathrm{d}\mathbf{R} \tag{21}$$

and to evaluate it, $P_{2\mathrm{HF}}$ has to be approximated.

7. The key step then follows. CS introduce a Taylor expansion through second-order

$$\int \frac{\exp(-\beta^2r^2)}{r}F(\mathbf{r},\mathbf{R})\mathrm{d}\mathbf{r} = 4\pi F(0,\mathbf{R}) \times\int_0^\infty \exp(-\beta^2r^2)r\mathrm{d}r + \frac{2\pi}{3}\nabla_r^2F(\mathbf{r},\mathbf{R}))_{r=0} \times\int_0^\infty \exp(-\beta^2r^2)r^3\mathrm{d}r \tag{22}$$

Here $F(\mathbf{r},\mathbf{R})$ should be interpreted as $P_{2\mathrm{HF}}(\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{R}-\frac{\mathbf{r}}{2})$. Recall that $P_{2\mathrm{HF}}(\mathbf{R},\mathbf{R}) = \frac{\rho^2}{2}$ and $\beta = q\rho^{1/3}$. Detailed algebra, using (20) then gives

8.

$$E_c = -\frac{\pi}{q^3}\int \rho(\mathbf{r})G(\beta,K)\mathrm{d}\mathbf{r} \tag{23}$$

where

$$G(\beta,K) = \frac{0.121 - 0.0167W + 0.0458/\beta - 0.005W/\beta}{1+1.1284/\beta+0.3183\beta^2} \tag{24}$$

and $W = K\beta^{-2}$ with

$$K = 2\frac{(\nabla_r^2P_{2\mathrm{HF}}(\mathbf{R}+\frac{\mathbf{r}}{2};\mathbf{R}-\frac{\mathbf{r}}{2}))_{r=0}}{\rho^2(\mathbf{R})} \tag{25}$$

9. This formula for $G(\beta,K)$ in the expression (23) for E_c suggests an approximation for the key part of (21)

$$\int \frac{P_{2\mathrm{HF}}(\mathbf{r_1},\mathbf{r_2})}{P_{2\mathrm{HF}}(\mathbf{R},\mathbf{R})}\Bigl(2\exp(-\beta^2r^2)\Bigl(1-\Phi(\mathbf{R})\Bigl(1+\frac{r}{2}\Bigr)\Bigr) - \exp(-2\beta^2r^2)\Bigl(1-\Phi(\mathbf{r})\Bigl(1+\frac{r}{2}\Bigr)\Bigr)^2\Bigr)\frac{\mathrm{d}\mathbf{r}}{r} = \frac{4\pi}{\rho}a\frac{1+bW\exp(-c\beta)}{1+d/\beta} \tag{26}$$

The parameters a, b, c, d are determined from a calculation using the He 1s HF orbital. The exact value of the left hand side was evaluated for ten values of R. Recall that for He $P_{2\mathrm{HF}} = 2(1s^2(r_1)\,1s^2(r_2))$. In our view this is the vital step. A justifiable form has been found for the correlation component of E_c, and adjustable parameters have been optimised using information on the HF density of He, for various values of the distance from the nucleus.

10. The final result is

$$E_\mathrm{C} = -0.04918\int \rho(\mathbf{R})\frac{1+0.173W\exp(-0.58/\beta)}{1+0.89/\beta}\mathrm{d}\mathbf{R} \tag{27}$$

with $\beta = 2.29\rho^{1/3}(\mathbf{r})$ and $W = 0.3814\rho^{-8/3}\bigl(\nabla_r^2P_{2\mathrm{HF}}\bigl(\mathbf{R}+\frac{\mathbf{r}}{2};\mathbf{R}-\frac{\mathbf{r}}{2}\bigr)\bigr)_{r=0}$. CS showed that their expression gave excellent values for the correlation energy of He, Be and Ne. They also determined the correlation energy of H_2O, which was too small by 8%, but we now understand that the left–right component was missing.

(b) The abstract to the LYP paper says "A correlation energy formulae due to CS, in which the correlation energy density is expressed in terms of the electron density and a Laplacian of the second order HF density matrix, is restated as a formula involving the density and the local kinetic energy density. On insertion of gradient expansions for the latter term, a density functional formulae is obtained for the correlation energy". "It is demonstrated that this formula gives atomic correlation energies within a few percent". In a little detail LYP gave the formulae

$$[\nabla_r^2P_{2\mathrm{HF}}(\mathbf{R},\mathbf{r})]_{r=0} = \rho(\mathbf{R})[t_\mathrm{HF}(\mathbf{R}) - 2t_W(\mathbf{R})] \tag{28}$$

$$t_W(\mathbf{R}) = \frac{1}{8}\frac{|\nabla\rho(\mathbf{R})|^2}{\rho(\mathbf{R})} - \frac{1}{8}\nabla^2\rho \tag{29}$$

$$t_\mathrm{HF}(\mathbf{R}) = C_F\rho(\mathbf{R})^{5/3} + [\frac{1}{9}t_W(\mathbf{R}) + \frac{1}{18}\nabla^2\rho] \tag{30}$$

the final formula holding to second order. LYP extended the formulae to a general UHF determinant. This makes it clear that the primary paper was CS; however, it is to the great credit of LYP that they brought CS to notice, and that their great knowledge of formal DFT enabled them to convert the CS expression into a GGA correlation functional.

(c) MSSP used partial integration ($\int F\nabla^2\rho\mathrm{d}\mathbf{r} = -\int\nabla F\cdot\nabla\rho\mathrm{d}\mathbf{r}$) to eliminate $\nabla^2\rho$, (which is numerically difficult) to obtain the final result

Table 1 The binding energies D_e of small molecules, calculated by HF, OPTX and OLYP, in kcal mol^{-1} [13]

Mol	D_e (obs)	D_e (HF)	D_e (OPTX)	ΔD_e (LYP)	D_e (OLYP)	Error
N_2	228.6	115.2	162.5	61.6	224.1	4.5
O_2	120.5	33.1	94.6	35.8	130.4	−9.9
F_2	38.5	−37.1	21.3	19.6	40.9	−2.4
H_2O	232.2	155.5	179.6	52.0	231.7	0.5
C_2H_4	562.6	428.5	447.0	115.5	562.5	0.1
C_2H_2	405.4	293.6	322.2	81.7	403.9	1.5

The values obtained with BLYP are very similar

$$\begin{aligned}E_c = {} & -a\int\frac{4}{1+d\rho^{-1/3}}\frac{\rho_\alpha\rho_\beta}{\rho}\mathbf{dr} - ab\\ & \times\int\omega\bigg(\rho_\alpha\rho_\beta\bigg[2^{11/3}C_F(\rho_\alpha^{8/3}+\rho_\beta^{8/3})\\ & +\left(\frac{47}{18}-\frac{7}{18}\delta\right)|\nabla\rho|^2-\left(\frac{5}{2}-\frac{1}{18}\delta\right)\\ & \times\left(|\nabla\rho_\alpha|^2+|\nabla\rho_\beta|^2\right)-\frac{\delta-11}{9}\\ & \times\left(\frac{\rho_\alpha}{\rho}|\nabla\rho_\alpha|^2+\frac{\rho_\beta}{\rho}|\nabla\rho_\beta|^2\right)\bigg]-\frac{2}{3}\rho^2|\nabla\rho|^2\\ & +(\frac{2}{3}\rho^2-\rho_\alpha^2)|\nabla\rho_\beta|^2+(\frac{2}{3}\rho^2-\rho_\beta^2)|\nabla\rho_\alpha|^2\bigg)\mathbf{dr}\end{aligned} \tag{31}$$

where

$$\omega = \frac{\exp(-c\rho^{-1/3})}{1+d\rho^{-1/3}}\rho^{-11/3} \tag{32}$$

$$\delta = c\rho^{-1/3}+\frac{d\rho^{-1/3}}{1+d\rho^{-1/3}} \tag{33}$$

$$C_F = \frac{3}{10}(3\pi^2)^{2/3} \tag{34}$$

and $a = 0.04918$, $b = 0.132$, $c = 0.2533$, $d = 0.349$, which are the CS values. MSSP verified that this functional gave good atomic correlation energies.

9 The success of GGA DFT

It was results of the following quality which convinced practising quantum chemists of the value of this DFT (Table 1).

10 Observations

1. It was the accuracy of such results (with BLYP) which turned the attention of quantum chemists to DFT.
2. The LYP contributions can be related to the number of electron pairs created on bond formation.
3. Standard ab initio quantum chemistry could not compete. MP2 needs enormous basis sets to obtain the shape of the wavefunction near the electron–electron cusp. The cost of this DFT is less than HF. Correlation has been and is the bugbare of quantum chemistry. At one swoop the need for the many electron wavefunction to obtain electron correlation effects was removed.
4. I hope it is clear from this presentation that the functionals BLYP and OLYP are not semi-empirical functionals. Parameters have been determined from atomic data only, no molecule is mentioned. This the great strength of these simple functionals, and surely explains their great success!
5. Can the CS–LYP–MSSP dynamical correlation functional be improved? We think so. We think that the form of the functional is plausible, for the reasons given in their derivation. Furthermore, the values for the molecular dissociation energies given in the table are good, but of course these are energy differences, not absolute energies. We think that the four parameters *a*, *b*, *c*, *d* could be readjusted. Following our successful work [5], where the exchange functional OPTX was determined by fitting to HF atomic energies, we suggest that the parameters could be determined by fitting to the atomic correlation energies of He–Ar. (the parameter in β does not need adjustment, as it can be absorbed into *c*, *d*). This may well enhance the predictive accuracy of the BLYP or OLYP functionals.

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