

A simple DFT-based diagnostic for nondynamical correlation

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Abstract We propose a simple DFT-based diagnostic for nondynamical correlation effects, namely $A_\lambda = (1 - \text{TAE}[X_\lambda C] / \text{TAE}[XC]) / \lambda$ where TAE stands for the molecular total atomization energy, XC is a pure-DFT exchange-correlation functional, and $X_\lambda C$ represents the corresponding hybrid with $100\lambda\%$ Hartree–Fock-type exchange. The diagnostic is a good predictor for sensitivity of energetics to the level of theory, unlike most wavefunction-based diagnostics. For GGA functionals, A_λ values approaching unity indicate severe nondynamical correlation, while values between 0 and about 0.1 indicate systems where correlation is predominantly dynamical in character (or entirely absent). The diagnostic is only weakly sensitive to the basis set (beyond polarized valence double zeta) and can easily be applied to problems beyond the practical reach of wavefunction ab initio methods

required for other diagnostics. We also propose a simple measure for the importance of dynamic correlation.

Keywords Nondynamical correlation · Density functional theory · Diagnostics · Ab initio · Thermochemistry

1 Introduction and background

When the Hartree–Fock reference determinant offers a very good zero-order description of the system, and no individual determinants or group of determinants make large contributions to the correlated many-body wavefunction, the molecule is said to be dominated by dynamical correlation. In such a scenario, the cluster expansion of the wavefunction converges rapidly, and a “gold standard” correlation method like CCSD(T) [1] truly comes very close to the exact (i.e., full CI) basis set correlation energy.

Deviations from this regime are, in the literature, interchangeably referred to as nondynamical correlation [2],¹ static correlation, near-degeneracy correlation, left-right correlation, and multireference effects [3].

In a very recent paper, Hollett and Gill (HG) [3] distinguish two types of nondynamical correlation, which they term Type A and B, while they designate dynamical correlation “Type D.” A similar dichotomy was proposed earlier by Scuseria and Tsuchimoshi (ST) [4] who use the labels “left-right strong correlation” and “angular strong correlation,” respectively, instead of “type A” and “type B”.

“Type A static correlation,” viz. “left-right strong correlation,” is best illustrated by stretching H_2 to infinite

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¹ The terms “dynamical” and “nondynamical” correlation appear to have been introduced first in Sinanoglu [2].

distance with RHF orbitals. Near r_e , the SCF wavefunction is an excellent zero-order description: as the bond is stretched, the σ_g and σ_u orbitals approach degeneracy, and eventually only a bideterminantal wavefunction will be an adequate zero-order approximation: a single-reference calculation using RHF orbitals will at large distance correspond to $H^+ + H^-$. However, as first noticed by Pople [5, 6], using UHF [7] orbitals not only are a lower energy obtained, but also correct dissociation is achieved: the single determinant is no longer an eigenfunction of the S^2 operator but is able to capture some of the static correlation. Some systems exhibit such a “UHF instability” [8] even at their (experimental or high-level ab initio) equilibrium geometries: examples can be found in the first data column of Table 4.

Type A correlation energy is often, confusingly, referred to as “long-range” correlation: dispersion between noble gas atoms, which is purely dynamical in character, is of course likewise a long-range effect, albeit in a quite different way.

“Type B static correlation,” viz. “angular strong correlation,” is best illustrated [3] by comparing the correlation energy of helium-like ions with arbitrary Z with the valence correlation energy of beryllium-like ions, likewise with arbitrary Z [9]. In the He-like case, the $1s$ orbital never becomes quasidegenerate with any other, and Hartree–Fock is a good zero-order description throughout: in the limit for large Z , the “type D” (purely dynamical) correlation energy converges to a constant [10, 11]. In the Be-like case for $Z < 4.138$, the absolute energy gap between the $2s$ and $2p$ orbitals is small and a UHF instability exists. As Z is increased above the “isostability point” $Z = 4.138$, the gap actually widens in absolute terms but becomes ever smaller *relative* to the actual orbital energies: In fact, the correlation energy in the large- Z limit contains a term that goes up linearly with Z (!). As the type D correlation will asymptotically approach a constant like for the He series, type B static correlation will become the dominant contribution for large Z .

It may be clear in a qualitative sense how nondynamical correlation is defined, or at least experienced quantum chemists have an intuitive grasp of it [12].² However, for assessing the quality of quantum chemical predictions or the need for more computationally demanding ones, a quantitative or at least semiquantitative definition would be very helpful. Several such “multireference diagnostics” or “nondynamical correlation diagnostics” have been proposed over the years by wavefunction ab initio

practitioners. These can basically be divided into two categories: wavefunction based and energy based. Values of various diagnostics for a representative selection of molecules can be found in Table 1, while those for the entire W4-11 set can be found in the Electronic Supporting Information.

Another perspective is offered by considering “Type A nondynamical correlation”/“left-right strong correlation” as a manifestation of quantum entanglement. A physically motivated measure of the latter is the von Neumann entropy [13], or the closely related correlation entropy [14, 15]

$$S_2 = - \sum_i \binom{n_i}{2} \ln \frac{n_i}{2} \quad (1)$$

where the n_i are the natural orbital occupation numbers. (Note that for a closed-shell, single-determinant Hartree–Fock wavefunction, $S_2 = 0$ since all n_i are either 2 or 0, and application of l’Hôpital’s rule yields $\lim_{x \rightarrow 0^+} x \ln x = 0$.) Partitioning in spatial and spin correlation entropies has also been considered [16].

Entanglement is the central concept in the DMRG (density-matrix renormalization group) community [17]. In a recent study [18] on correlation effects in polycyclic aromatic hydrocarbons (PAHs), Mazziotti and coworkers employ Eq. (1) as a diagnostic for static correlation. They note that, as written, the expression is not intensive: As a workaround, applying it to CASSCF expansions for PAHs of different sizes, they truncated summations at the core and Rydberg ends of the CASSCF window such that they have the same number of NOs in each summation.

Out of the wavefunction-based diagnostics, perhaps the most widely used one is the T_1 diagnostic of Lee and Taylor [19], which is essentially nothing but the Frobenius norm of the single-excitation amplitude vector divided by the square root of the number of electrons correlated, $T_1 = \|\mathbf{t}_1\|_2 / \sqrt{n}$. (The denominator ensures that T_1 is approximately size-intensive.) Empirically, a T_1 of greater than 0.02 is said to indicate significant nondynamical correlation effects [16]. A closely related quantity is the D_1 diagnostic [20–22] of Janssen and Nielsen, which is the matrix norm of \mathbf{t}_1 . T_1 is not foolproof by itself: for example [23], F_2 has a deceptively low $T_1 = 0.011$ despite being a notoriously “multireference” molecule (it is actually metastable at the SCF level), and $T_1 = 0.027$ for ozone only suggests mild problems for what is in fact a pathological system.

As for the largest T_2 amplitude in a CCSD calculation—another wavefunction-based diagnostic fairly widely employed in the coupled cluster community—it is actually larger for formaldehyde than for dioxygen (a much harder system to “get right”). Monitoring both T_1 and the largest T_2 amplitudes viz. C_2 coefficients will in practice detect

² Intuitive, empirical grasp of a concept was memorably expressed by Associate Justice Potter Stewart in the US Supreme Court decision in *Jacobellis versus Ohio* [12]: “Perhaps I could never succeed in intelligibly [defining it]. But I know it when I see it.”

Table 1 Diagnostics for representative sample of W4-11 set, sorted by ascending %TAE[$T_4 + T_5$]

	T1diag nostic	D1diag nostic	Truhlar Mdiag	CASSCF 1- C_0^2	$-\Delta E_{\text{valFCI}}$	valFCI 1- C_0^2	Largest T2	n_{HDOMO}	n_{LUMO}	$A_{25\%}$ [PBE]	%TAE [SCF]	%TAE [[T]]	%TAE [post(T)]	%TAE [T_4+T_5]
H ₂	0.006	0.008	0.024	0.012	0.039	0.018	-0.056	1.976	0.024	0.011	76.6	0	0	0
H ₂ O	0.007	0.011	0.022	0.022	0.003	0.002	-0.048	1.978	0.023	0.116	68.8	1.5	-0.01	0.09
CF ₄	0.011	0.030	0.027	0.053	0.013	0.006	-0.022	1.978	0.032	0.205	69.2	2.8	-0.08	0.13
C ₂ H ₆	0.008	0.013	0.024	0.071	0.011	0.008	-0.032	1.975	0.023	0.028	78.5	0.9	-0.01	0.03
C ₂ H ₄	0.011	0.032	0.071	0.084	0.024	0.030	-0.119	1.929	0.072	0.057	77.4	1.3	0.00	0.08
C ₂ H ₂	0.013	0.028	0.064	0.089	0.045	0.041	-0.084	1.937	0.064	0.104	74.4	2.1	0.02	0.2
CO	0.019	0.039	0.047	0.057	0.045	0.039	-0.067	1.955	0.050	0.206	70.2	3.1	0.04	0.26
CO ₂	0.018	0.047	0.049	0.079	0.065	0.050	-0.063	1.962	0.060	0.244	66.5	3.6	0.01	0.28
N ₂	0.013	0.026	0.062	0.072	0.067	0.051	-0.095	1.941	0.065	0.305	52.6	4.2	0.17	0.51
SO ₂	0.021	0.056	0.080	0.083	0.056	0.060	-0.091	1.934	0.093	0.404	47.0	6.1	0.16	0.66
N ₂ O	0.020	0.048	0.076	0.108	0.110	0.083	-0.086	1.937	0.088	0.462	35.3	7.0	0.24	0.8
P ₄	0.018	0.037	0.058	0.144	0.078	0.097	-0.046	1.950	0.066	0.207	42.0	7.6	-0.20	0.94
NO ₂	0.025	0.065	0.113	0.107	0.091	0.086	-0.093	1.925	0.112	0.543	26.2	8.5	0.47	0.95
O ₂	0.007	0.013	0.080	0.060	0.063	0.054	-0.101	1.960	0.045	0.551	22.2	7.7	0.47	1.04
F ₂ O	0.015	0.040	0.094	0.093	0.094	0.075	-0.069	1.913	0.100	1.052	-32.2	14.6	0.95	1.58
FOOF	0.026	0.087	0.147	0.153	0.159	0.162	-0.069	1.872	0.166	1.098	-32.0	16.9	1.19	1.68
C ₂	0.038	0.086	0.403	0.291	0.146	0.234	-0.293	1.595	0.401	0.657	12.6	13.3	0.27	1.83
B ₂	0.039	0.076	0.350	0.215	0.081	0.176	-0.288	1.665	0.303	0.578	30.7	14.7	2.13	2.05
BN	0.073	0.199	0.283	0.218	0.094	0.189	-0.224	1.716	0.281	0.850	-10.9	18.8	-0.33	2.2
S ₄	0.022	0.088	0.262	0.210	0.106	0.195	-0.185	1.766	0.290	0.451	31.4	12.2	1.01	2.2
FO ₂	0.043	0.142	0.256	0.166	0.120	0.184	-0.170	1.786	0.256	0.949	-16.7	15.3	2.24	2.33
F ₂	0.011	0.029	0.131	0.067	0.061	0.055	-0.169	1.872	0.133	1.393	-79.5	19.5	1.66	2.46
O ₃	0.027	0.077	0.223	0.169	0.157	0.160	-0.192	1.797	0.243	1.007	-30.6	17.4	1.95	2.87

ΔE_{valFCI} is in Hartree, the remaining values are dimensionless

most problematic systems but for instance (see Table 1), the fairly mild scores of F₂O₂ (a.k.a. FOOF) on both criteria belie its highly problematic [24] character.

Another diagnostic that has been used over the years are the natural orbital occupations of the highest occupied and lowest virtual orbitals. The “ M diagnostic” of Truhlar and coworkers [25] effectively condenses these into a single number:

$$M = \frac{1}{2} \left(2 - n_{\text{HDOMO}} + n_{\text{LUMO}} + \sum_{j \text{ SOMO}} |n_j - 1| \right) \quad (2)$$

where n_i stands for the natural orbital (generalized) occupation number of orbital j , and, in a single-determinant picture, HDOMO would be the highest doubly occupied molecular orbital, LUMO the lowest unoccupied molecular orbital, and the SOMOs any singly occupied molecular orbitals. For the special case of 2-in-2 CASSCF on a closed-shell singlet, this reduces to $M = n_{\text{LUMO}}$, which, with $x = n_{\text{LUMO}}$, is also the low- x limit of the corresponding correlation entropy $S_2 = -(x/2) \ln(x/2) - (1 - x/2) \ln(1 - x/2)$.

Yet another criterion, known in various guises among people who carry out multireference calculations, is the

coefficient C_0 (or its corresponding weight C_0^2) in a CISD or full-valence CASSCF wavefunction [26]. Since actually their deviation from unity is the true criterion, we report the CASSCF $1 - C_0^2$ in Table 1 instead. These two are not bulletproof, as the low $1 - C_0^2$ and moderate M for F₂ illustrate.

Various energetic criteria for nondynamical correlation were proposed by one of us [23] in an attempt to find reliable measures for inadequacy of the CCSD(T) method. Earlier, Handy and coworkers [27] proposed $E[\text{CASSCF, full valence}] - E[\text{SCF}]$, while Krylov et al. [28] proposed $E[\text{full CI, valence}] - E[\text{SCF}]$. These latter two definitions differ through the orbital relaxation involved in CASSCF.

As an operational definition, we proposed [23] %TAE[$T_4 + T_5$], that is, the percentage of the molecular total atomization energy accounted for by connected quadruple and quintuple excitations. These are obtained a posteriori as a by-product of accurate W4 theory [23, 29] computational thermochemical calculations, but in view of their immense cost (the corresponding steps account for the lion’s share of the CPU time in a typical W4 calculation), these are obviously not useful a priori predictors. We did find two energy-based a priori diagnostics (requiring no more than a CCSD(T)/cc-pVTZ single point calculation)

that are statistically very strongly correlated with %TAE[$T_4 + T_5$], namely %TAE[(T)] ($R^2 = 0.941$) and %TAE[SCF] ($R^2 = 0.810$). These latter statistics were obtained over a sample of 34 molecules spanning a wide range of multireference character: more recently, this analysis was repeated over the 140 molecules in the W4-11 benchmark dataset [30]: Upon elimination of the anomalous Be_2 diatomic (which is unbound at the CCSD level), we found essentially identical R^2 values of 0.94 and 0.80, respectively. This study also considered the basis set dependence of these diagnostics and found that they did not change significantly upon basis set expansion beyond cc-pVTZ [31]. It was also found [23, 30] that the T_1 and D_1 diagnostics correlate fairly poorly with %TAE[$T_4 + T_5$], with $R^2 = 0.36$ and 0.33, respectively, over the W4-11 set.

The reader might wonder why not use %TAE[post-CCSD(T)], that is, %TAE[$T_4 + T_5$] + %TAE[CCSDT – CCSD(T)], as a benchmark instead. However, the good performance of CCSD(T) itself results [32, 33] from a (mildly erratic) error compensation between T_4 (which universally increases TAE) and $T_3 - (T)$ (which almost universally decreases it), and hence highly problematic molecules like singlet C_2 look much more “well-behaved” on this criterion than they actually are.

The issue of nondynamical correlation not only vexes wavefunction ab initio practitioners, but also bedevils the presently much larger DFT developer and especially user community as well. While DFT is generally more resilient toward nondynamical correlation than, for example, many-body perturbation theory, it is common knowledge that, for example, “pure DFT” and hybrid DFT methods may yield very different answers in such multireference systems as early transition metal complexes.

As DFT (at least below the fifth rung of Jacob’s Ladder [34]³) is a single-determinant theory, diagnostics based on the structure of the multideterminantal wavefunction require additional wavefunction calculations, as do the %TAE[SCF] and %TAE[(T)] diagnostics. However, while preparing a lecture about the adiabatic connection [35] and hybrid DFT methods [36] for a graduate-level computational chemistry course, an alternative suggested itself, which is the subject of the present paper.

³ In this Biblical metaphor (Gen. 28:10–19) introduced by Perdew and Schmidt [34], Heaven is the exact solution and Earth the Hartree product. The first rung represents the local density approximation, the second rung generalized gradient approximations, the third rung meta-GGAs involving higher derivatives of the density, the fourth rung occupied-orbital-dependent functionals (of which hybrids are a special case), and the fifth rung virtual-orbital-dependent functionals (of which double-hybrids [56–58] are a special case).

2 Methods

As our benchmark dataset, we used the 140 molecules in the W4-11 set, at fixed reference geometries taken from the supporting information to Ref. [30]. All calculations were performed on the Linux cluster of CASCaM (Center for Advanced Scientific Computing and Modeling) at the University of North Texas. CASSCF [37], valence-only full CI, and CCSD(T) calculations were carried out using the MOLPRO 2010.1 package [38] using full-valence active spaces in a cc-pVTZ basis set; for some of the largest molecules such as acetic acid, the lowest valence orbitals and the corresponding antibonding virtuals were taken out of the active space for technical reasons. For the open-shell systems, restricted open-shell wavefunctions were used. All DFT calculations were carried out using the Gaussian 09 program system [39] on the same computational platform; here, unrestricted Kohn–Sham orbitals were used for the open-shell systems. Orbital stability analyses were likewise carried out using Gaussian 09.

Total atomization energies (TAE_e values) were obtained as differences between the molecular energy and the sum of those of the neutral atoms in their respective ground states.

%TAE[post-CCSD(T)] and %TAE[$T_4 + T_5$] were taken from the Electronic Supporting Information of the W4-11 paper [30].

The following five DFT exchange–correlation functionals were considered: SVWN5 [40], BLYP [41–43], PBE [44], BB95 [45], and TPSS [46].

Full numerical data for the W4-11 dataset are given in the Electronic Supporting Information to the present paper.

3 Results and discussion

One can plot a molecule’s total atomization energy and its various components (1-electron, Coulomb, exchange, correlation) as a function of the percentage of Hartree–Fock-like exchange. A representative such plot, for oxirane/ethylene epoxide ($\text{C}_2\text{H}_4\text{O}$), is given in Fig. 1. As can be seen there, while some components display just a hint of curvature, the dependence of both TAE and its various contributions exhibits surprisingly weak deviation from linearity. (It would be perfectly linear if the calculations were carried out in a post-LDA fashion.)

Zooming in a little, we do find that the ratio TAE(λ)/TAE(0) as a function of the fraction of HF exchange λ only shows some weak curvature (deviation from linearity) at the quadratic level (and essentially none at cubic and higher orders) for almost all the species. Even more conveniently, the dimensionless quantity $A_\lambda = (1 - \text{TAE}(\lambda)/\text{TAE}(0))/\lambda$ lends itself very well to linear regression to

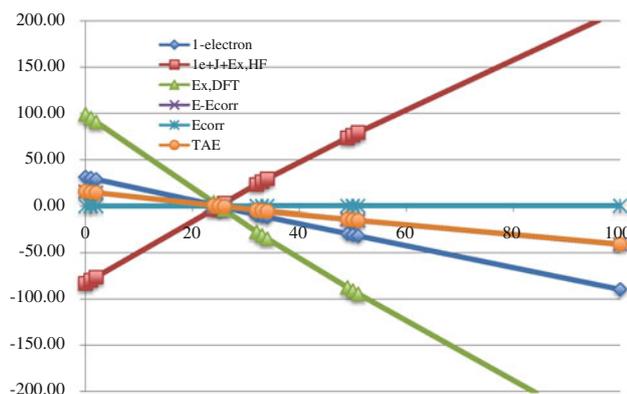


Fig. 1 Profile of different components to the $PBE_{\lambda}/cc\text{-pVTZ } TAE_e$ of oxirane as a function of the percentage of Hartree-Fock exchange. Values are in kcal/mol relative to $\lambda = 25\%$ (PBE0)

$A_{\lambda} \approx S_{\lambda} + T_{\lambda}\lambda$, with $R^2 = 0.99\text{--}0.9999$ across the board (see Electronic Supporting Information). Typically, and consistent with the near-linearity of the TAE dependence, we find T_{λ}/S_{λ} on the order of 0.1, with the exception of a few species for which S_{λ} is very small to begin with and which are dominated by dynamical correlation (such as H_2 and B_2H_6). Large values of S_{λ} are found for molecules the quantum chemist intuitively thinks of as “basket cases” such as F_2O_2 , O_3 , etc.

Qualitatively, the same behavior is seen for all exchange-correlation functionals considered, but on average, we find that $S_{\lambda}[PBE]/S_{\lambda}[LDA] = 0.44$ and $S_{\lambda}[TPSS]/S_{\lambda}[PBE] = 0.76$. It stands to reason that sensitivity to the

percentage of HF exchange would decrease as one walks up the “Jacob’s Ladder” [34]. $S_{\lambda}[BLYP]$ is very similar to $S_{\lambda}[PBE]$, and $S_{\lambda}[BB95]$ is almost indistinguishable from $S_{\lambda}[BLYP]$, suggesting not only that similar behavior is seen within rungs of Jacob’s Ladder but also that the exchange functional affects values more than the correlation functional.

As can be seen in Table 2, squared correlation coefficients between S_{λ} for the four non-LDA functional combinations are universally very large, $R^2 = 0.993\text{--}0.999$. This suggests that they all essentially contain the same information.

How well do the S_{λ} parameters correlate with the more traditional nondynamical correlation indices? Correlation is largest with %TAE[SCF], with which R^2 vary from 0.96 to 0.97, and second largest with %TAE[(T)], all functionals yielding R^2 around 0.90.

Considering %TAE[$T_4 + T_5$] as the benchmark, the best statistical predictor is not surprisingly %TAE[(T)] with $R = 0.97$, with %TAE[SCF] and S_{λ} tied for second place. When it comes to %TAE[post-CCSD(T)] (error compensations and all), the DFT-based diagnostic in fact marginally outperforms %TAE[SCF] and %TAE[(T)].

Of the wavefunction-based diagnostics, the only one that has a reasonable correlation with %TAE[$T_4 + T_5$] is Truhlar’s *Mdiag*, which for closed-shell species is effectively the average of HOMO and LUMO natural orbital occupations (as well as the low- n_i limit of the HOMO–LUMO correlation entropy). The T_1 diagnostic statistically correlates poorly with all energy-based diagnostics, except

Table 2 Squared correlation matrix of various diagnostics for nondynamical correlation for the W4-11 dataset less Be_2 (i.e., 139 molecules)

R^2 matrix	$S_{\lambda}[BB95]$	$S_{\lambda}[PBE]$	$S_{\lambda}[TPSS]$	$S_{\lambda}[BLYP]$	CASSCF $1-C_0^2$	valFCI Ecorr	valFCI $1-C_0^2$	CASSCF Mdiag	%TAE e[SCF]	%TAEe[(T)]	%TAEe[post(T)]	%TAEe[T_4+T_5]	T_1
$\lambda\lambda[BB95]$	1.000	0.999	0.989	0.998	0.214	0.465	0.455	0.401	0.962	0.900	0.607	0.791	0.343
$\lambda\lambda[PBE]$		1.000	0.991	0.999	0.211	0.458	0.447	0.393	0.964	0.904	0.597	0.792	0.328
$\lambda\lambda[TPSS]$			1.000	0.993	0.209	0.438	0.436	0.396	0.971	0.900	0.606	0.797	0.306
$\lambda\lambda[BLYP]$				1.000	0.214	0.455	0.450	0.405	0.967	0.908	0.615	0.802	0.327
CASSCF $1-C_0^2$					1.000	0.613	0.793	0.735	0.210	0.355	0.194	0.420	0.334
valFCI Ecorr						1.000	0.790	0.473	0.427	0.509	0.278	0.278	0.521
valFCI $1-C_0^2$							1.000	0.821	0.429	0.616	0.409	0.409	0.698
Mdiag								1.000	0.394	0.555	0.442	0.654	0.425
%TAEe[SCF]									1.000	0.896	0.589	0.805	0.286
%TAEe[(T)]										1.000	0.593	0.938	0.383
%TAEe[post-CCSD(T)]											1.000	0.674	0.339
%TAEe[T_4+T_5]												1.000	0.378
T_1													1.000

Between T_1 and D_1 , $R^2 = 0.895$; correlations of D_1 with other diagnostics in this table are similar to or lower than those for T_1 . For instance, with valFCI Ecorr and valFCI $1 - C_0^2$, $R^2 = 0.278$ and 0.312 , respectively

Unsurprisingly, the HOMO–LUMO correlation entropy tracks the CASSCF *Mdiag* very closely, with $R^2 = 0.953$

for the valence FCI correlation energy: its strongest correlation, aside from with the closely related D_1 , is seen with $1 - C_0^2$ from a valence full CI calculation. (We note in passing that $1 - C_0^2$, the Truhlar M diagnostic, and the HOMO–LUMO correlation entropy all appear to contain very similar information.)

For diagnostic purposes, one wonders whether we really need to plot and fit such “HF exchange response curves,” or can we, for a given fixed λ° , simply consider

$$A_{\lambda^\circ} = (1 - \text{TAE}(\lambda^\circ)/\text{TAE}(0))/\lambda^\circ \approx S_\lambda + \lambda^\circ T_\lambda$$

As T_λ is not only small but also itself fairly well correlated with $\% \text{TAE}[T_4 + T_5]$, $R = 0.75$ in the PBE case, we can expect the correlation coefficient of A_{λ° with $\% \text{TAE}[T_4 + T_5]$ to be pretty constant. Not surprisingly, for values of λ° ranging from 0.05 to 1 (i.e., 5–100 %), A_{λ° has an essentially constant $R = 0.888$ – 0.893 with $\% \text{TAE}[T_4 + T_5]$. We can, therefore, take a given arbitrary λ° , for example, 25%, in which case the equation reduces to $A_{25\%}[\text{PBE}] = 4(1 - \text{TAE}(\text{PBE0})/\text{TAE}(\text{PBE}))$ or $A_{25\%}[\text{BLYP}] = 4(1 - \text{TAE}(\text{BILYP})/\text{TAE}(\text{BLYP}))$.

(While the present paper was being prepared for submission, a paper by Truhlar and coworkers [47, 48] was brought to our attention, in which $B1 = (\text{BE}_{\text{BLYP}} - \text{BE}_{\text{BILYP}})/n_{\text{bonds}}$ was considered for bond-breaking reactions.)

Returning to Table 1, and to the full table for the W4-11 set given in supporting information, we can state the following (for PBE or BLYP):

- A_λ values around or above 1 appear to indicate severe-to-pathological static correlation
- values around 0.5 appear to indicate moderate-to-severe nondynamical correlation
- values near 0.3 appear to indicate moderate nondynamical correlation
- near 0.15: mild
- below about 0.10: correlation is primarily dynamic in character

One advantage of A_λ is its relatively low cost. The cc-pVTZ basis set may still be out of reach for many practical problems, however, and therefore, the basis set dependence of the diagnostic is of interest. Table 3 lists correlation coefficients and deviation statistics (from near-basis-set-limit values with Jensen’s pc-3 polarization consistent basis set [49–55]) for the LANL2DZ, 6-31G*, and 6-311G** basis sets. It is shown there that $R^2 \geq 0.98$ for basis sets of at least polarized double-zeta quality, while $R^2 \geq 0.995$ can be reached for triple-zeta double polarization or better basis sets. Only for small double-zeta basis sets like LANL2DZ or SDD could basis set dependence potentially become an issue.

Are we primarily dealing with Type A or Type B static correlation? One easy probe for that is to check for UHF

Table 3 Basis set sensitivity of $A_{50\%}[\text{PBE}]$ as measured by the squared correlation coefficient with pc-3 results

	R^2 with pc-3
LANL2DZ	0.8375
SDD	0.8657
6-31G*	0.9911
6-311G**	0.9913
6-311G(2d,p)	0.9953
cc-pVTZ	0.9976
def2-SVP	0.9840
def2-TZVPP	0.9985
pc-1	0.9870
pc-2	0.9979
pc-3	1 by def.

instabilities (Table 4). Stability analysis using Gaussian 09 for RHF references reveals RHF/UHF energy lowerings for 29 out of 139 molecules, plus for Be_2 and Be atom: of these, the following exceed 10 kcal/mol: Be_2 , $\text{BN}(^1\Sigma^+)$, $\text{C}_2(^1\Sigma_g^+)$, $\text{CH}_2(^1A_1)$, FOOF, O_3 , S_3 , and S_4 . Using B3LYP orbitals instead, only eight such instabilities are seen (three of which insignificant), which is reduced to just five (two of which insignificant) using BLYP orbitals. (The three species for which UBLYP is significantly lower in energy than RBLYP are the singlets BN, C_2 , and CH_2 .) This illustrates that, at equilibrium geometries, we are dealing chiefly with type B nondynamical correlation even with HF orbitals, and almost exclusively so using DFT orbitals. It also suggests that using DFT rather than HF orbitals as a reference (as is done, e.g., in double-hybrid functionals [56–58]⁴) imparts greater resilience to at least type A static correlation. In fact, Cohen and Handy argue [59–62] that the exchange functional in DFT includes “left-right correlation.” Huzak et al. [63] demonstrate that there is a clear analytical relationship between the extent of symmetry breaking and the inverse of the HOMO–LUMO gap. Note that in a Belgian collaboration on linear polyacenes [64], it was found that even naphthalene already exhibits a UHF instability, despite $\% \text{TAE}[\text{SCF}] = 75.5$ and $\% \text{TAE}[(T)] = 1.56$ values that are clearly in the “dynamical-dominated” range.⁵ In the present work, we find quite low $A_{25\%}[\text{PBE}]$ values of 0.067 and 0.075 for benzene and naphthalene, while the M_{diag} obtained from QCISD/cc-pVTZ natural orbitals are more “midrange” at 0.076 and 0.087, respectively. (The same holds true for the HOMO–LUMO correlation entropies.)

Finally, we note (Table 4) that both the absolute and the relative RHF/UHF energy lowerings exhibit fairly high

⁴ For the original concept of perturbation theory in a basis of Kohn–Sham orbitals, see: Görling and Levy [58].

⁵ In fact, even benzene is marginally UHF-unstable.

Table 4 UHF relaxation energy lowerings (kcal/mol) for the molecules in the W4-11 set

	HF	B3LYP	BLYP
AlH	0.33		
Be ₂	12.93	0.20	
Be	0.20		
BH	4.08	0.03	0.02
BN	53.44	6.30	3.81
C ₂ (1Σ ⁺ _g)	75.28	11.42	36.42
CCl ₂	4.45		
CF ₂	0.37		
CH ₂ C	0.42		
CH ₂ (¹ A ₁)	11.44	4.74	4.62
cis-HCOH	1.78		
cis-HONO	0.13		
cis-N ₂ H ₂	1.34		
dioxirane	1.12		
F ₂ O	0.07		
F ₂	6.27		
FOOF	24.96		
glyoxal	0.23		
HNO	3.50	0.18	0.12
NCCN	2.23		
O ₃	53.66	1.70	
oxirene	1.50		
P ₂	5.24		
S ₂ O	6.50		
S ₃	16.45		
S ₄ (c2v)	34.16	1.17	
tr-HCOH	1.26		
tr-HONO	0.29		
tr-N ₂ H ₂	1.21		

Absent entries mean the RHF solution is stable with respect to spin-symmetry breaking

For the values given, correlation coefficients with some diagnostics for nondynamical correlation are as follows: Truhlar $M_{\text{diag}} R = 0.923$; HOMO–LUMO correlation entropy $S_{\text{corr}} R = 0.905$; CASSCF $1 - C_0^2 R = 0.840$. Correlation coefficients between $(\text{TAE}[\text{UHF}] - \text{TAE}[\text{RHF}])/\text{TAE}$ total and various diagnostics are as follows: Truhlar $M_{\text{diag}} R = 0.875$, $S_{\text{corr}} R = 0.869$, CASSCF $1 - C_0^2 R = 0.778$, $\% \text{TAE}[(T)] R = 0.734$

correlation coefficients with the correlation entropy S_2 ($R = 0.905$ absolute, $R = 0.869$ relative) and with the (in fact, if perhaps not in intent) closely related M diagnostic. This again suggests that these diagnostics primarily measure type A static correlation, rather than the sum of both types A and B.

For the sake of completeness: what values of A_{λ° are obtained in situations where no correlation contribution at all is present? We considered two examples: $D_e[\text{H}_2^+]$ and $\text{IP}(\text{H})$. As neither has a correlation contribution of any kind, we expect A_{λ° values close to zero: in fact, we find $A_{25\%}[\text{PBE}] = +0.056$ and -0.011 , respectively, acceptably close to zero. $A_{25\%}[\text{BB95}] = 0.068$ and -0.003 , respectively, $A_{25\%}[\text{BLYP}] = 0.068$ and -0.004 , respectively, while for $A_{25\%}[\text{TPSS}]$, we find 0.074 and 0.000, respectively.

A reviewer inquired whether the M06L [65], M06 [66], M06-2X [66], and M06HF [67] family of functionals could be used for this diagnostic. Since the meta-GGA exchange and correlation parts of the M06 family [68] include dozens

of adjustable parameters optimized over the training set at the given percentages of Hartree–Fock exchange (which are 0, 28, 56, and 100, respectively), the dependence of TAEs on the percentage of HF exchange is much weakened, as illustrated in Ref. [69, 70] for the BMK functional proposed there.

Defining $A_{\text{M06}} = (1 - \text{TAE}[\text{M06}]/\text{TAE}[\text{M06L}])/0.28$ and similarly for $A_{\text{M06-2X}}$ and $A_{\text{M06-HF}}$, and applying this to the W4-11 set, we find small negative values for systems dominated by dynamical correlation, rising to positive values in the 0.2–0.4 range for systems with severe static correlation. The correlation coefficients with $\% \text{TAE}[T_4 + T_5]$ are 0.79 for A_{M06} , 0.84 for $A_{\text{M06-2X}}$, and 0.85 for $A_{\text{M06-HF}}$. These are lower than for, for example, $A_{25\%}[\text{PBE}]$ but still indicate somewhat useful predictive power, which may be useful for people carrying out application studies primarily using the M06 family (Table 3).

Finally, one might wonder whether a simple, convenient indicator for the importance of *dynamical* correlation could be generated from DFT data. If we eliminate the molecules with $\%[(T)]$ above 10% (i.e., cases with strong static correlation), we can consider, for a given correlation functional C ,

$$D[C] = 1 - \text{TAE}[\text{HF}]/\text{TAE}[\text{HFC}]$$

where HF stands for straight Hartree–Fock, and HFC for the combination of pure Hartree–Fock exchange with DFT correlation functional C . $D[C]$ has the following squared correlation coefficients R^2 with $\% \text{TAE}[\text{SCF}]$: $D[\text{LYP}]$ 0.907, $D[\text{PBE}]$ 0.927, $D[\text{TPSS}]$ 0.887, and $D[\text{B95}]$ 0.948. If instead we consider the percentage of TAE accounted for by CCSD—which in the limit for a system with only dynamical correlation approaches the *entire* correlation contribution—then the R^2 values slightly increase to 0.923, 0.935, 0.902, and 0.952, respectively. Values for the W4-11 set can be found in the Electronic Supporting Information. We note that the idea of using DFT correlation functional using HF orbitals as a measure of dynamical correlation was, to the best of our knowledge, first suggested by Handy and coworkers [59, 60].

4 Conclusions

We propose a simple DFT-based diagnostic for nondynamical correlation effects, namely $A_\lambda = (\text{TAE}[XC] - \text{TAE}[X_\lambda C])/\lambda \text{TAE}[XC]$ where TAE stands for the molecular total atomization energy, XC is a pure-DFT exchange–correlation functional, and $X_\lambda C$ represents the corresponding hybrid with $100\lambda\%$ Hartree–Fock-type exchange. The diagnostic is a good predictor for sensitivity of energetics to the level of theory, unlike most wavefunction-based diagnostics. $A_\lambda =$ values approaching unity indicate severe

nondynamical correlation, while values between 0 and about 0.1 indicate that correlation is predominantly dynamic in character. The diagnostic converges rapidly with any basis set of polarized double-zeta or better quality and can easily be applied to problems beyond the practical reach of wavefunction ab initio methods required for other diagnostics.

We also can propose a simple gauge for the importance of dynamical correlation in a molecular binding (or reaction) energy: $D[C] = 1 - \text{TAE}[\text{HF}]/\text{TAE}[\text{HFC}]$. Both indices can be computed with just three calculations: for example, using the BLYP exchange-correlation combination, one could make do with just BLYP, HFLYP, and HF calculations if $A_{100} \%[\text{BLYP}]$ is acceptable, and an additional B1LYP calculation if $A_{25} \%[\text{BLYP}]$ is preferred.

As a final remark, in the context of the present special issue, it might be observed that the present diagnostic touches on the area of conceptual density functional theory, which has been the focus of intense research activity in Belgium [71–73].

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