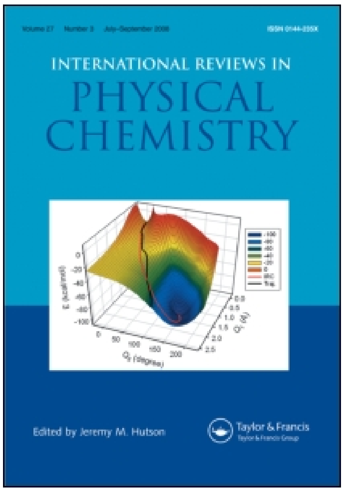

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A charge-excitation approach to through-bond interactions

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The functional groups at which nucleophilic or electrophilic substitution or addition occur in organic molecules may be considered as charge traps in the charged-radical transient (intermediate or transition) states which play a crucial part in such reactions. The role of the sigma framework in modifying the electronic properties of the functional-group trapping states may be referred to as sigma coupling. The general expressions for sigma coupling are derived in the context of a charge-excitation model for the transient species. They provide a quantitative definition of Hoffmann's through-bond concept.

1. Introduction

Localized functional groups (e.g. lone pairs, non-conjugated ethylenic units) play a crucial role in determining the reactivity of molecules in reactions involving charged *transient* species (i.e. intermediates or transition states). They are usually the sites at which nucleophilic or electrophilic substitution or addition occurs. The functional group behaviour may be modified electronically (as distinct from sterically) through variation of the sigma framework to which it is attached. The definition of the coupling between such localized functional groups and the sigma framework is therefore of fundamental chemical interest. The earliest discussion of such coupling may be traced back to the hyperconjugation ideas of Mulliken (1939); more recently, it has been reformulated in terms of though-bond coupling (Hoffmann 1971).

Hoffmann's through-bond concept derives explicitly from the consideration of the interaction between *two* functional groups, arising from the coupling of both groups to a common sigma framework; strictly speaking, the classification does not consider the effect of the coupling of an individual group to the sigma framework, which we shall refer to as sigma coupling. In Hoffmann's original analysis, the predominantly functional-group MOs of the reactant (as distinct from transient) species contain contributions from the sigma MOs which may be considered as arising from a functional-group MO/sigma MO 'interaction'. This *orbital interaction* is the origin of through-bond coupling in such a scheme. The link to reactivity (and hence to the properties of the transient species) then proceeds through the usual Frontier MO-type arguments (Fukui 1971). The through-bond concept has enjoyed a wide popularity, especially in the area of photoelectron spectroscopy (Bock and Ramsey 1973, Wittel and McGlynn 1977, Paddon-Row 1982).

The charged transient states may be treated directly through charge-delocalization models in which the charge is effectively treated as an excitation. This stems initially from the work of Hall (1951) and Lennard-Jones and Hall (1952), in which the cationic radical states of alkanes were described by transforming delocalized MO solutions to a localized (equivalent) basis. Pauzet *et al.* (1972) treated similar systems, but started with a localized-bond basis. Their calculations are effectively *ab initio*. In this work, these ideas are extended to cationic or anionic radical states in a general way, and the analysis further broadened to include functional groups explicitly. The delocalized excitation solutions are developed as a linear superposition of localized charge structures, each of which describes a localization of the charge in a particular bond or functional group. The functional group in this context serves as a charge or excitation trap, and the role of the sigma framework may be considered as (i) stabilizing the trapped localized charge state through sigma polarization and (ii) partially delocalizing the excitation over the sigma framework itself (sigma coupling).

Such an excitation treatment is ideally suited to an analysis of through-bond coupling for a number of reasons. Firstly, it treats the transient species directly, instead of through an indirect analysis of the orbitals of the reactant species. Secondly, it is possible to differentiate between charge (excitation) delocalization, and the delocalization arising from the incorporation of electron interchange symmetry (interchange delocalization). Such a differentiation is obscured in the conventional MO treatment based on the reactant species, the treatment on which the work of Hoffmann and Fukui is ultimately based. It will in fact be shown that only a limited degree of interchange delocalization is required. The sigma-coupling contributions can then be isolated directly by a judicious use of perturbation theory in mixing the sigma-localized states with those of the functional groups. The through-bond coupling in turn can then be expressed in terms of additive sigma couplings of the individual functional groups. The resulting expressions are amenable to analysis in terms of local, coulombic interactions (resulting directly from the relatively localized interchange, and the excitation treatment), rather than the more abstract notions of 'orbital interactions' of the delocalized MO procedures based on the reactant species. Above all, the formalism closely follows the 'arrow pushing' approaches of mechanistic organic chemistry, and as such may be considered as at least narrowing the interface between the formalistic approach of theory and the widely-accepted conceptual framework of experimentalists in treating such problems.

2. The model

The *reactant* is modelled as having n_s two-electron, sigma-bond orbitals $\{\psi_s\}$, and a set of n_f functional-group orbitals $\{\psi_f\}$, each doubly occupied. The totality of these localized orbitals (LOs) will be denoted by $\{\psi_i\}$, $i=1,\ldots,n_s+n_f$. Any other electrons are represented only through leading to an effective core charge on each nucleus; these core charges act collectively in setting up an attractive potential v_c for the $2(n_s+n_f)$ 'valence' electrons. The total hamiltonian H for such a system may be written in the form

$$H=h+v, \quad h=\sum_{\nu} k_e(\nu)+\sum_{\nu} v_c(\nu)+v_c^0, \quad v=\sum_{\substack{\nu,\mu \\ \nu<\mu}} v(\mu,\nu) \tag{1}$$

where h contains all the one-electron terms: viz. k_e is the kinetic energy operator of the relevant electron; v_c is the effective core potential; and v_c^0 the core–core repulsions. v contains all the electron–electron repulsion terms.

We shall not be concerned here with the determination of an 'optimal' set of LOs, and impose only the constraint of orthonormality. (A non-orthogonal localized basis is readily Löwdin-orthogonalized (Löwdin 1951), which for small overlaps retains the local nature of the basis.) The justification of orthonormality or, at the very least, small overlaps of the LOs follows for the sigma-bond overlaps by noting that bond orbitals formed from pure sp^3 hybrids are rigorously orthogonal; for the functional-group/sigma-bond case, the overlap integrals are usually small simply on the basis of separation of the relevant groups. The imposition of orthonormality permits the exploitation of the ZDO (zero differential overlap) approximation, first introduced by Parr (1952) and still widely used in approximate MO methods (Pople and Beveridge 1970); viz. that for the two-electron integrals,

$$\langle\psi_i(1)\psi_j(2)|v|\psi_k(1)\psi_l(2)\rangle=\gamma_{ij}\delta_{ik}\delta_{jl} \tag{2}$$

This approximation is consistent with a drastic simplification in the incorporation of electron interchange symmetry, a crucial feature of the analysis that follows.

The ground state of the *reactant* species is written in the form

$$|\Psi^0\rangle=\mathscr{A}\prod_k|k\bar{k}\rangle,\quad k=1,\ldots,n_s+n_f \tag{3}$$

where $|k\bar{k}\rangle=\psi_k(v_k)\alpha(v_k)\psi_k(v_k')\beta(v_k')$, and $\mathscr{A}$ is the antisymmetrizer. It is significant that the energy corresponding to the fully antisymmetrized function of equation 3 is, after making the ZDO approximation, identical to that obtained by putting $\mathscr{A}=1$; i.e. any electron interchange between electrons in different LOs may be rigorously neglected in the determination of the ground-state energy within the ZDO approximation. The resultant energy expression has the form

$$E_0=\sum_k\{2h_{kk}+\gamma_{kk}+\sum_{j\neq k}2\gamma_{jk}\} \tag{4}$$

where

$$h_{kk}=\langle\psi_k(1)|h|\psi_k(1)\rangle \tag{5}$$

All these integrals have simple classical interpretations: h_{kk} is the kinetic energy and the attractive core potential energy of an electron in ψ_k; γ_{kk} is the repulsion between two electrons in ψ_k; and γ_{kj} is the repulsion between electrons in ψ_k and ψ_j.

2.1. *Localized charge* (*LC*) *states*

We are concerned here not with the reactant state, but rather the charged-radical states formed by removing or adding an electron. The determination of these states proceeds in a number of stages, of which the definition of an LC state is the first. The cation-radical LC state formed by removing an electron from the LO indexed by i may be written (allowing no relaxation at this stage)

$$|i^+\rangle=\left(\prod_{k\neq i}|k\bar{k}\rangle\right)|i\rangle \tag{6}$$

whereas the anion-radical LC state formed by adding an electron to the lowest excited LO ψ_{i^*} has the form

$$|i^-\rangle=\left(\prod_k|k\bar{k}\rangle\right)|i^*\rangle \tag{7}$$

Although for completeness we shall take antisymmetrization to be implied in both equations (6) and (7) above, for most purposes the specific product forms will indeed suffice.

Such LC states may be denoted in a general way by $|i^c\rangle$ ($c=\pm1$) and, for the purposes of determining the energy within the ZDO approximation corresponding to such a state, antisymmetrization may be ignored completely. The energy has the form $E_i^{0c} = \langle i^c|H|i^c\rangle$ so that

$$E_i^{0+} = E_0 - h_{ii} - \gamma_{ii} - 2\sum_{k\neq i} \gamma_{ik} \tag{8}$$

$$E_1^{0-} = E_0 + h_{i^*i^*} + 2\sum_k \gamma_{i^*k} \tag{9}$$

The LC states may now be considered as 'relaxing' in two distinct stages: (i) the sigma-polarization stage, and (ii) the charge-delocalization stage. The former retains the localization of the charge on a given site, whereas the latter will be considered in the next section as it leads to the final delocalized solutions.

The sigma-polarization stage involves the relaxation of the sigma electrons by the localized charge; i.e. repolarization. Formalistically, it may be accommodated by mixing in excited configurations of the form

$$|i^c\rangle|j\rangle^{-1}|j^*\rangle, \quad j\neq i \tag{10}$$

where the notation $|j\rangle^{-1}$ omits j from the preceding product and replaces it with j^*. Such corrections have been discussed in detail for cationic alkanes by Pauzat *et al.* (1972). For our purposes, it is sufficient to note that such configurations are of significantly higher energy than $|i^c\rangle$, and may be incorporated by perturbation theory. The effect on the energy may be approximated in the form

$$E_i^c = E_i^{0c} - \sum_{j\neq i} \frac{e^2\bar{\alpha}_j}{2r_{ij}^4} \tag{11}$$

where use has been made of the multipole expansion (charge-dipole terms) and the sum over the excitation manifold for a particular j incorporated into an average bond or functional-group polarizability. The effect of the repolarization is to lower the energy of each LC state, and generally in a relatively uniform manner (i.e. the repolarization energy may be taken to be independent of i in many cases).

The correction to the wavefunction need not be considered here, provided the matrix element $\langle i^c|H|i^c\rangle$ is replaced by E_i^c wherever it appears. This is because the corrections to the LC functions lead to negligible contributions to the off-diagonal matrix elements which are discussed in the next section.

2.2. *Delocalized charge (DC) states*

The individual LC states are now used as a basis for the variational determination of the solutions of H in the form

$$|\Psi_\alpha^c\rangle = \sum_i C_{i\alpha}|i^c\rangle \tag{12}$$

These solutions represent a superposition of the LC 'structures' with weightings that are directly related to the probability of finding the charge at a particular site, and will be referred to as delocalized charge (DC) solutions. The diagonal matrix elements of H are given by equation (11). The off-diagonal matrix elements may be determined as follows. For $c = +1$, the evaluation of the matrix element $\langle i^+|H|j^+\rangle$ within the ZDO approximation requires antisymmetrization for the electrons on sites i and j, but any other electron interchanges may be rigorously ignored; i.e.

$$|i^+\rangle=\left(\prod_{k\neq i,j}|k\bar{k}\rangle\right)\mathscr{A}_{ij}|j\bar{j}i\rangle \tag{13}$$

$$|j^+\rangle=\left(\prod_{k\neq i,j}|k\bar{k}\rangle\right)\mathscr{A}_{ij}|i\bar{i}j\rangle \tag{14}$$

Then

$$\langle i^+|H|j^+\rangle=-h_{ij}=-\langle\psi_i(1)|h|\psi_j(1)\rangle \tag{15}$$

For $c=-1$, the corresponding matrix element within the ZDO approximation requires no antisymmetrization at all, leading to

$$\langle i^-|H|j^-\rangle=h_{i^*j^*}=\langle\psi_{i^*}(1)|h|\psi_{j^*}(1)\rangle \tag{16}$$

The interpretation of these off-diagonal terms proceeds through the definition of the exchange density

$$\rho_{ij}(r)=\int\psi_i^\dagger(r')\psi_j(r')\delta(r-r')\,dr' \tag{17}$$

which constitutes (in units of electronic charge) a real charge density associated with an electron transfer between ψ_i and ψ_j. The h_{ij} integrals then describe the classical coulombic interaction between this exchange density and the core charges. It is significant that the overlap integral, which is the integrated exchange density, is taken to vanish. This is, however, quite consistent with a non-vanishing h_{ij}, which simply requires the *distribution* of the exchange density to be such that a net interaction can occur. This is an important feature of our analysis, as Hoffmann's 'orbital interactions' are usually discussed in terms of overlaps, whereas the relevant quantities are really the h_{ij} integrals. We refer to the h_{ij} integrals as transfer integrals.

The drastic approximations in the interchange symmetry used above indicate that interchange delocalization for the anion radical states may be neglected entirely, the electron (the excitation in this case) hopping fron one site to the next through the transfer integrals of the excited LOs. For the cation-radical states, the interchange delocalization extends only between the two sites between which the positive charge (i.e. the hole) is transferred. The process may therefore be visualized as a simple back electron transfer.

3. Functional-group solutions

We now turn to the determination of the sigma coupling using the preceding analysis. Instead of determining the totality of DC states in single variation step (equation (12)), the total manifold of orthonormal LC solutions is partitioned into a sigma LC manifold $\{|s^c\rangle\}$, $s=1,\ldots,n_s$ and a functional-group LC manifold $\{|f^c\rangle\}$, $f=n_s+1,\ldots,n_s+n_f$. It is important to remember that each LC state is a multi-electron state, and not like the 'one-electron' functions of MO schemes. We first determine the set of 'unperturbed' sigma DC solutions in which the excitation is constrained to move only on the sigma framework; these may be defined as the solutions

$$|\sigma^c\rangle=\sum_s C_{s\sigma}|s^c\rangle \tag{18}$$

which are determined variationally using the *full* hamiltonian but the subspace of sigma LC solutions, yielding the eigenvalues

$$E^c_\sigma = \sum_s C^2_{s\sigma} E^c_s + \sum_{\substack{s,s' \\ s \neq s'}} C_{s\sigma} C_{s'\sigma} h_{ss'} \tag{19}$$

The 'unperturbed' functional-group DC solutions may be determined in a similar manner; i.e.

$$|\phi^c\rangle = \sum_f C_{f\phi} |f^c\rangle \tag{20}$$

with eigenvalues

$$E^c_\phi = \sum_f C^2_{f\phi} E^c_f + \sum_{\substack{f,f' \\ f \neq f'}} C_{f\phi} C_{f'\phi} h_{ff'} \tag{21}$$

The solutions to H in terms of the full LC basis may now be determined by writing the hamiltonian in the subspace of the totality of sigma and functional group DC solutions; i.e. in the form

$$H = H^0 + V \tag{22}$$

where

$$H^0 = \sum_\phi E^c_\phi |\phi^c\rangle\langle\phi^c| + \sum_\sigma E^c |\sigma^c\rangle\langle\sigma^c| \tag{23}$$

$$V = \sum_{\phi,\sigma} H_{\phi\sigma}(|\phi^c\rangle\langle\sigma^c| + |\sigma^c\rangle\langle\phi^c|) \tag{24}$$

and

$$H_{\phi\sigma}\lambda = \langle\phi^c|H|\sigma^c\rangle \tag{25}$$

The very nature of a functional group is such that its LC states are appreciably lower in energy than those of the sigma states. It follows that there will be a set of solutions localized largely on the functional groups which may be approximated using perturbation theory as

$$|\phi^c\rangle' \simeq |\phi^c\rangle - \sum_\sigma \frac{\langle\sigma^c|h|\phi^c\rangle}{(E^c_\sigma - E^c_\phi)} |\sigma^c\rangle \tag{26}$$

$$E'^c_\phi \simeq E^c_\phi - \sum_\sigma \frac{|\langle\sigma^c|h|\phi^c\rangle|^2}{(E^c_\sigma - E^c_\phi)} \tag{27}$$

where

$$\langle\sigma^c|h|\phi^c\rangle = \sum_f \sum_s C_{f\phi} C_{s\sigma} h_{sf} \tag{28}$$

These equations define the sigma-coupling contributions to the functional-group wavefunctions and energies in the most general perturbative form. For cation-radical states, the transfer integrals are defined for 'ground-state' LOs, whereas for anion-radical states, they are defined for the 'excited' LOs.

4. Applications

We consider the particular application to the cation-radical states of non-conjugated dienes of the type studied in detail by Paddon-Row (1982), illustrated in figure 1.

The energies of the cation-radical states are readily probed through photoelectron spectroscopy. For theoretical simplicity, we consider a pair of ethylenic groups labelled f_1 and f_2, separated by a single *trans* chain of n_s sigma bonds labelled $s=1,\ldots,n_s$. (Generalization to include the whole sigma framework is formalistically trivial.) This is illustrated in figure 2 for the case when $n_s=4$.

The determination of the 'unperturbed' sigma DC solutions proceeds through the use of equations 18 and 19 and the approximations

$$\langle s^c|H|s^c\rangle = E_s^c = \varepsilon \quad \text{for all } s \tag{29}$$

and

$$\begin{aligned}\langle s^c|H|s'^c\rangle &= \eta \quad && \text{if } s, s' \text{ nearest neighbours}\\ &=0 && \text{otherwise.}\end{aligned} \tag{30}$$

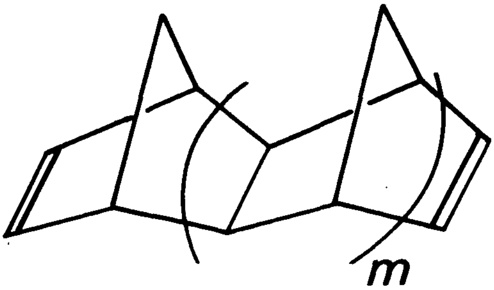

Figure 1. The non-conjugated dienes studied by Paddon-Row (1982). In theoretically modelling the system, the effect of only one of the most direct sigma chains ($n_s=m+2$) is considered.

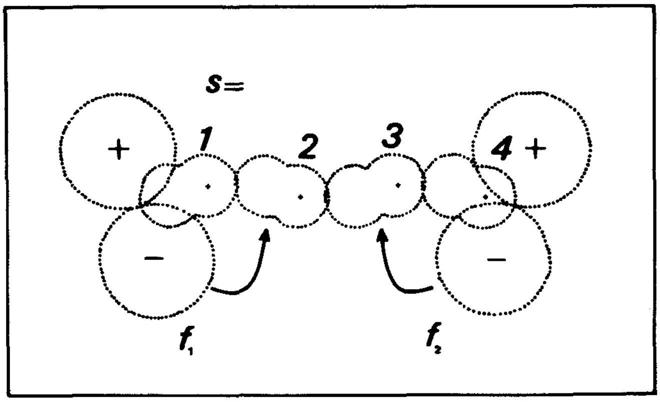

Figure 2. The model system for two functional groups f_1, f_2 separated by $n_s=4$ carbon–carbon bonds. The reference phases are shown. Note that the transfer integrals between f_1 and $s=1$, f_2 and $s=4$ vanish by symmetry, but that finite integrals exist with $s=2$ and $s=3$ respectively as indicated by the arrows.

The resultant solutions are analytic: viz.

$$C_{s\sigma}=2^{1/2}(n_s+1)^{-1/2}\sin\frac{\sigma s\pi}{(n_s+1)} \tag{31}$$

$$E_\sigma^+=\varepsilon+2\eta\cos\frac{\sigma\pi}{(n_s+1)} \tag{32}$$

The lowest-energy solution ($\sigma=n_s$) has the coefficients of equation 31 having a maximal sign alternation with respect to s. This follows from noting that as illustrated in figure 3, the exchange density for two LOs formed from sp^3 hybrids has a negatively-charged region (positive exchange density) encapsulating a positively-charged core which dominates the interaction leading to the transfer integral; i.e. $h_{s,s+1}<0$ and $\eta>0$. This sigma DC state lies closest to the reactant ground state in energy, and thus has the lowest ionization energy.

The 'unperturbed' functional-group solutions have the form

$$|\phi^+(\pm)\rangle=2^{-1/2}(|f_1^+\rangle\pm|f_2^+\rangle),\quad E_\phi^+(\pm)=E_f^+ \tag{33}$$

We consider the perturbed DC solutions in two stages. Firstly, we assume that only the functional group f_1 is present, which will have a rigorously vanishing transfer integral with $s=1$, but not for the bond $s=2$, for which

$$\langle f_1|h|s=2\rangle=\xi \tag{34}$$

With all other transfer integrals set to zero, the perturbed energy in the *absence* of the other group f_2 has the form

$$E_\phi'^+\simeq E_f^+ +\sum_\sigma S_f^+(\sigma,n_s) \tag{35}$$

where

$$S_f^+(\sigma,n_s)=-2\xi^2(n_s+1)^{-1}(E_\sigma^+-E_f^+)^{-1}\sin^2\frac{2\pi\sigma}{(n_s+1)} \tag{36}$$

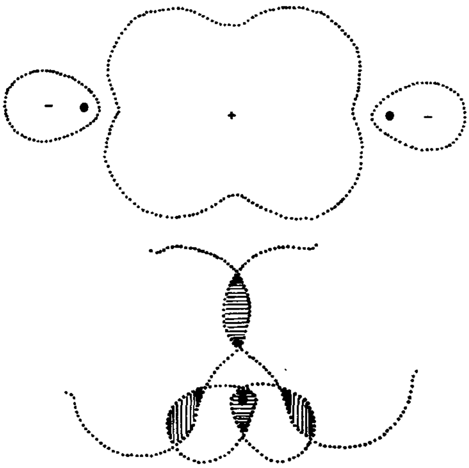

Figure 3. (Above) A sigma-bond LO (localized orbital) with relative phases shown. The heavy dots represent carbon cores. (Below) The exchange density between two neighbouring sigma LOs. A positive exchange density (real negative charge) is shown with horizontal shading, the vertical shading being negative.

The $S^{+}_{f}(\sigma, n_s)$ may be defined as the sigma coupling of the single functional group f_1 with the particular sigma DC state labelled by σ.

For both functional groups present, with f_2 having a finite transfer integral only with respect to the sigma bond $s = n_s - 1$, the perturbed functional group solutions take the form, using equations 27 and 33,

$$E'^{+}_{\phi}(\pm) \simeq E^{+}_{f} + \frac{1}{2}\sum_{\sigma} S^{+}_{f}(\sigma, n_s)\{1 \pm (-1)^{\sigma+n_s+1}\}^2 \tag{37}$$

It follows that the $\phi^{+}(-)$ state will be lowered by $2S^{+}_{f}(\sigma, n_s)$ if $(\sigma + n_s + 1)$ is odd, not affected if it is even. The reverse applies for the $\phi^{+}(+)$ state. The resulting interaction of the $\phi^{+}(-), \phi^{+}(+)$ states with different symmetry sigma states leads to an energy splitting of the functional-group states. It is precisely this splitting which is usually ascribed to through-bond coupling. The above expression highlights the origin of the through-bond coupling as a simple superposition of the sigma couplings of the individual groups; whether the superposition is 'constructive' or 'destructive' depends simply on the form of the functional-group DC state.

Some qualitative comparisons with experimental results (Paddon-Row *et al.* 1981, Paddon-Row 1982) support the general features of the model. Experimentally, the ionization energies are split on either side of that of the compound with only one functional group, as expected on the basis of equations 35 and 37. The 'parity rule' follows from the n_s-dependence in the $\{1 \pm (-1)^{\sigma+n_s+1}\}^2$ factor. The dependence of the pi-splitting on the sigma chain length may be extracted by considering only the sigma-coupling with the lowest-energy sigma DC state: i.e.

$$S^{+}_{f}(n_s, n_s) \propto \left\{\sin^2 \frac{2\pi}{(n_s+1)} \bigg/ (n_s+1)\right\} \simeq [4\pi^2/(n_s+1)^3] \quad \text{as} \quad n_s \to \infty.$$

This agrees quantitatively with the slow attentuation of through-bond effects with increasing n_s. The correct factor in curly brackets has the values 0·18, 0·09, 0·02 for $n_s = 4$, 6, 11 respectively, whereas the limiting function in square brackets has the corresponding values 0·32, 0·12, 0·02; thus the limiting $(n_s + 1)^{-3}$ behaviour is already dominant for relatively low n_s values.

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