

Exchange and Correlation in Density Functional Theory and Quantum Chemistry

MICHAEL J. G. PEACH,^{1,2} DAVID J. TOZER,¹ NICHOLAS C. HANDY³

¹Department of Chemistry, University of Durham, Durham DH1 3LE, United Kingdom

²Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

³Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom

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ABSTRACT: The nature of exchange, dynamic correlation (DC) and left–right correlation (LRC) is considered in density functional theory and wavefunction-based quantum chemistry. The presence of LRC in approximate exchange density functionals is highlighted and the separation of LRC and DC is considered. For H₂, the Heitler–London approach is shown to include the essential elements of exchange and LRC. The arguments are illustrated by a comparison of Gaussian orbital s-optimised Heitler–London and OPTX potential energy curves. They agree well near equilibrium, but differ at large distances due to the inability of the OPTX form to describe the dissociation process. LRC and DC values determined using the two approaches are compared. The influence of higher angular momentum functions in the Heitler–London approach is then investigated (commonly called self-consistent valence bond); the agreement with OPTX degrades, leading to a larger value of LRC and a smaller value of DC at H₂ equilibrium. © 2009 Wiley Periodicals, Inc. *Int J Quantum Chem* 111: 563–569, 2011

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1. Introduction and Definitions

Following the Kohn and Sham [1] partitioning of the total electronic energy, the exchange–correlation functionals of density functional theory (DFT) model exchange and correlation,

which include a small kinetic energy component. For the uniform electron gas, the exchange and correlation components are determined independently. Many common approximations also combine independently determined exchange and correlation terms, such as the classic Becke–Lee–Yang–Parr (BLYP) generalised gradient approximation (GGA) functional, which is the sum of the Becke 1988 exchange functional (B88X) [2] and the Lee–Yang–Parr (LYP) correlation functional [3], and the

Correspondence to: M. J. G. Peach; e-mail: m.j.g.peach@durham.ac.uk

Perdew–Burke–Ernzerhof exchange and correlation GGA functionals [4], which are determined from exact conditions. The exchange and correlation components in least-squares refined functionals however are usually determined dependently; examples include the B3LYP [2, 3, 5–7] hybrid functional and the Hamprecht–Cohen–Tozer–Handy (HCTH) [8] GGA. The latter class of functionals can be very reliable for molecules similar to those in the fitting data. Despite achieving reasonable accuracy near equilibrium, most functionals provide a poor description of the dissociation process, which can be attributed to their inability to describe systems with locally fractional spins or electron-numbers [9].

In the present study, we consider the nature of the exchange and correlation components of the exchange–correlation energy and investigate possible connections between these DFT quantities and wavefunction-based quantum chemistry (QC) quantities within spin-restricted closed shell systems.

The exchange energy is defined exactly within Hartree–Fock theory as

$$E_x[\rho] = \left\langle \Psi_0 \left| \hat{V}_{ee} \right| \Psi_0 \right\rangle - J, \quad (1)$$

where Ψ_0 is the Hartree–Fock single determinant wavefunction, \hat{V}_{ee} is the electron–electron interaction operator and J is the Coulomb energy determined using Ψ_0 . Following Löwdin [10], the correlation energy is then the negative quantity $E(\text{Corr}) = E(\text{FCI}) - E(\text{HF})$, where $E(\text{FCI})$ is the full configuration interaction (FCI) electronic energy, and $E(\text{HF})$ is the Hartree–Fock energy. In density functional theory, the exchange energy is again defined as Eq. (1), but in this case Ψ_0 is the noninteracting Kohn–Sham single determinant. The DFT and HF exchange energies are not exactly the same, since the former uses a multiplicative potential in the orbital equations, although in practice they are very close.

The correlation energy is then defined as

$$E(\text{Corr})[\rho] = T - T_s + V_{ee} - J - E_x[\rho] \quad (2)$$

with T the kinetic energy, T_s the kinetic energy associated with the Kohn–Sham noninteracting system and where V_{ee} is the full electron–electron interaction energy. For the present study, we consider partitioning the correlation energy into two components: dynamic correlation (DC) and left–right correlation (LRC).

1.1. DYNAMIC CORRELATION

DC is best understood as a short-range effect, arising from the reduction in probability as two electrons approach one another, due to electron–electron repulsion. It is a nondirectional effect in first order. Higher terms such as $r_{12}r_{1A}r_{2B}$ will be directional, where r_{12} is the distance between two electrons. A wavefunction that does not include r_{12} , either explicitly or implicitly, does not have this correlation. Examples that do include it are the Hylleraas wavefunction for He [11–13], which explicitly includes r_{12} , and the configuration interaction (CI) wavefunction for Be with the two configurations $1s^22s^2$ and $1s^22p^2$. Simple mathematics shows that these two configurations introduce $\mathbf{r}_1 \cdot \mathbf{r}_2$, which by the cosine formula includes r_{12}^2 .

The Hylleraas wavefunction also includes terms such as r_1r_2 , which are often referred to as “in–out” or “radial” correlation. These are again effects arising from the reduction in probability. In CI such terms are introduced through determinants involving unoccupied orbitals with the same symmetry as the occupied orbitals in a Hartree–Fock (HF) picture. DC includes both radial and angular correlation.

1.2. LEFT–RIGHT CORRELATION

LRC ensures that molecules dissociate to their constituent atoms, necessary because in nearly all cases HF wavefunctions do not correctly describe this dissociation. It is a directional effect, and is necessarily long-range in nature. The simplest molecule to discuss is H_2 , for which it is well-known that the valence bond (VB) wavefunction of Heitler and London (HL) [14] does provide a correct description of dissociation—away from the united atom, it can be rigorously proven that the two configuration multiconfigurational self-consistent field (MCSCF) wavefunction is equivalent to the VB wavefunction. The most common approach for including LRC is through the $\sigma_g^2 \rightarrow \sigma_u^2$ configurations. However, such an MCSCF wavefunction may also include DC (for example, at the united atom limit, the energy is slightly below Hartree–Fock).

Insight into LRC can be gained through a consideration of H_2 at molecular dissociation, where the kinetic contribution to the exchange–correlation energy is zero and the exchange energy is equal in magnitude to the total correlation energy. At this point the DC contribution is also zero (two noninteracting single-electron atoms), so the correlation energy is entirely left–right. The nature of this correlation can be understood through an examination of the exchange–correlation hole

at molecular dissociation. For Hartree–Fock (HF) wavefunctions, the exchange-only hole is delocalised over the atomic centres; for FCI wavefunctions, the exchange–correlation hole is localised around the electron. The effect of LRC is therefore to convert a delocalised exchange hole into a localised exchange–correlation hole. In the local density approximation (LDA), it may be shown [15] that the exchange hole is $9\rho_\sigma j_1^2(k_F s)/(k_F s)^2$, where $s = r_{12}$, $j_1(x)$ is the first order spherical Bessel function and $k_F = (6\pi^2\rho_\sigma)^{1/3}$. This exchange hole is therefore localised and so, despite being an ‘exchange’ functional, the LDA effectively introduces LRC in multicentre systems. Since all exchange functionals include a significant proportion of LDA exchange, it follows that all exchange functionals automatically introduce some LRC. The role of the correlation functional in DFT is therefore to return the remaining contributions to the total electronic energy as defined in Eq. (2).

1.3. SEPARATION OF DC AND LRC

In contrast to the case of H_2 at infinite separation, the LRC is zero for an isolated atom by our definition since they have only one centre; therefore all the correlation is dynamic. Atomic Kohn–Sham calculations using a DFT exchange-only functional should not introduce any LRC. Therefore, exchange functionals should closely reproduce exact exchange energies for atoms. Becke recognized this when he determined his B88X exchange functional through a fit to the ground-state Hartree–Fock energies of He, Ne, Ar, Kr and Xe,

$$\text{B88X} = -C_X \sum_\sigma \int \rho_\sigma^{4/3}(\mathbf{r}) d\mathbf{r} - \beta \sum_\sigma \int \frac{x_\sigma^2 \rho_\sigma^{4/3}(\mathbf{r})}{1 + 6x_\sigma \beta \sinh^{-1}(x_\sigma)} d\mathbf{r} \quad (3)$$

with $\beta = 0.0042$, $x^2 = |\nabla\rho|^2\rho^{-8/3}$, $C_X = \frac{3}{4}(\frac{6}{\pi})^{1/3}$. Cohen and Handy [16] subsequently determined an exchange functional (OPTX) that was refined by least squares to give the HF energies of the 18 atoms H–Ar,

$$\text{OPTX} = -1.05151C_X \sum_\sigma \int \rho_\sigma^{4/3}(\mathbf{r}) d\mathbf{r} - 1.43169 \sum_\sigma \int \rho_\sigma^{4/3}(\mathbf{r}) u_\sigma^2 d\mathbf{r} \quad (4)$$

with $u = \gamma x^2/(1 + \gamma x^2)$, $\gamma = 0.006$. The mean absolute difference between B88X and Hartree–Fock is

just 7.40 kcal mol^{−1}. Between OPTX and Hartree–Fock it is only 3.56 kcal mol^{−1}; OPTX is a high quality exchange functional for light atoms (see for instance Refs. [17, 18]).

Colle and Salvetti [19] determined their correlation functional from a correlated wavefunction for He, and so (following our definitions above) it should return just DC. Recently Colle [20] performed KS calculations using the associated correlation potential, added on to the HF operator; he obtained near FCI energies for these atoms.

For general molecular systems, it is not possible to uniquely separate DC and LRC. Functionals such as B88X and LYP suffer from this, due to the absence of appropriate data describing the separate energy contributions in the dissociation process.

This study considers several separations in an attempt to gain insight into the requirements of exchange and correlation functionals in DFT. Given the link to molecular dissociation, we shall define the LRC by

$$E(\text{LRC}) = E(\text{LRX}) - E(\text{HF}) \quad (5)$$

where LRX is any method which satisfies the requirement that it can correctly dissociate a molecule (i.e., includes LRC) and includes exchange, but which does not contain any r_{12} dependence. The associated dynamic correlation energy is then defined by the requirement that

$$E(\text{LRC}) + E(\text{DC}) = E(\text{Corr}). \quad (6)$$

2. The Heitler–London Wavefunction

As a starting point, consider the valence bond (VB) Heitler–London (HL) wavefunction in the H_2 molecule,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, v_1, v_2) = [\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) + \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2)] \times [\alpha(v_1)\beta(v_2) - \beta(v_1)\alpha(v_2)] \quad (7)$$

where ϕ_A, ϕ_B are atomic orbitals centred on the protons A and B. If $\phi_A = 1s_A$, $\phi_B = 1s_B$, then Ψ is the classic HL [14] wavefunction. Using symmetry, the variational energy expression for Ψ is

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{h_{AA}S_{AA} + h_{AB}S_{AB} + (AA|BB) + (AB|AB)}{S_{AA}^2 + S_{AB}^2} + \frac{1}{R_{AB}} \quad (8)$$

where

$$h_{AA} = \left(\phi_A \left| -\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} \right| \phi_A \right) \quad (9)$$

$$h_{AB} = \left(\phi_A \left| -\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} \right| \phi_B \right) \quad (10)$$

$$S_{AA} = (\phi_A | \phi_A) \quad (11)$$

$$S_{AB} = (\phi_A | \phi_B). \quad (12)$$

We observe that the molecule dissociates correctly (i.e., includes LRC) and the energy expression involves the exchange integral, divided by overlap integrals which are invariant upon scaling. It does not depend on r_{12} so does not contain DC. The HL wavefunction therefore satisfies our requirements for an LRX method.

We also observe that, upon coalescence, the wavefunction can revert to the Hartree–Fock wavefunction for the united atom (He). The HL binding energy is only 3.20 eV compared with the HF binding energy of 3.64 eV.

2.1. THE WANG WAVEFUNCTION

The HL wavefunction using $\phi_A = 1s_A$, $\phi_B = 1s_B$ is not optimal for an arbitrary bond length. Wang [21] instead let $\phi_A = \exp(-\zeta r_A)$, $\phi_B = \exp(-\zeta r_B)$, and optimised the parameter ζ . He obtained a binding energy of 3.79 eV. Handy recently observed [22] that the Wang electronic energy is close to the OPTX electronic energy at several bond lengths, consistent with the fact that both approaches include exchange and some degree of left–right correlation.

We further investigate this idea in the present work. However, rather than using a single optimised Slater s function, we set

$$\phi_A(\mathbf{r}) = \sum_p d_p \exp(-\alpha_p r_A^2) \quad (13)$$

$$\phi_B(\mathbf{r}) = \sum_p d_p \exp(-\alpha_p r_B^2) \quad (14)$$

and minimised E with respect to (d_2, d_3, \dots) using a simple minimiser. We used the s function coefficients from the cc-pV8Z Gaussian basis set in an uncontracted manner ($\alpha_p = 1.0, 0.05, 0.11, 0.23, 0.49, 1.08, 2.48, 6.08, 16.0, 44.7, 126.6, 290.4, 623.3, 1903.2, 3471.4, 13940.8$).

Figure 1 compares the H_2 potential energy (PE) curves determined using the QC methodologies Hartree–Fock, FCI, Wang, and the DFT methodology OPTX. Extensive basis sets are used throughout.

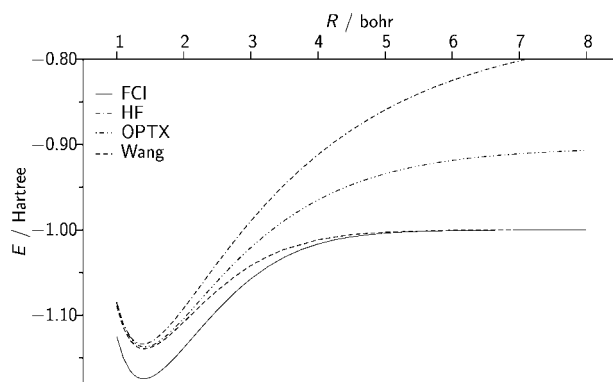


FIGURE 1. Potential energy curves for H_2 calculated by the QC methodologies HF, FCI, Wang, and the DFT methodology OPTX.

Near equilibrium, Wang and OPTX yield similar energies, which are below Hartree–Fock but above FCI; the Wang and OPTX bond lengths of 1.409 and 1.419 a_0 are slightly longer than the Hartree–Fock and FCI values of 1.386 and 1.401 a_0 . The lower energies and longer bonds from Wang/OPTX, compared to Hartree–Fock, reflect the presence of LRC in these methods; the subsequent introduction of DC would lower the energy further and shorten the bond length. At larger distances the Wang curve dissociates correctly, whereas the form of OPTX precludes this.

These results are in line with those reported by Cohen et al. [23] in calculations on atoms, where they say that ‘dynamic correlation is often thought to be associated with reduction in size because it allows electrons to arrange themselves in the most efficient manner possible’ and ‘left–right correlations are responsible for an increase in molecular size, with a greater effect on molecular shape than dynamic correlation’.

If we define LRX in Eq. (5) to be the Wang approach then we obtain the following LRC and DC contributions:

$$E(\text{LRC}) = E(\text{Wang}) - E(\text{HF}) \quad (15)$$

$$E(\text{DC}) = E(\text{FCI}) - E(\text{Wang}). \quad (16)$$

These quantities are plotted in Figure 2(a) for H_2 , as a function of R . Figure 2(b) presents the analogous DFT quantities

$$E(\text{LRC}) = E(\text{OPTX}) - E(\text{HF}) \quad (17)$$

$$E(\text{DC}) = E(\text{OLYP}) - E(\text{OPTX}). \quad (18)$$

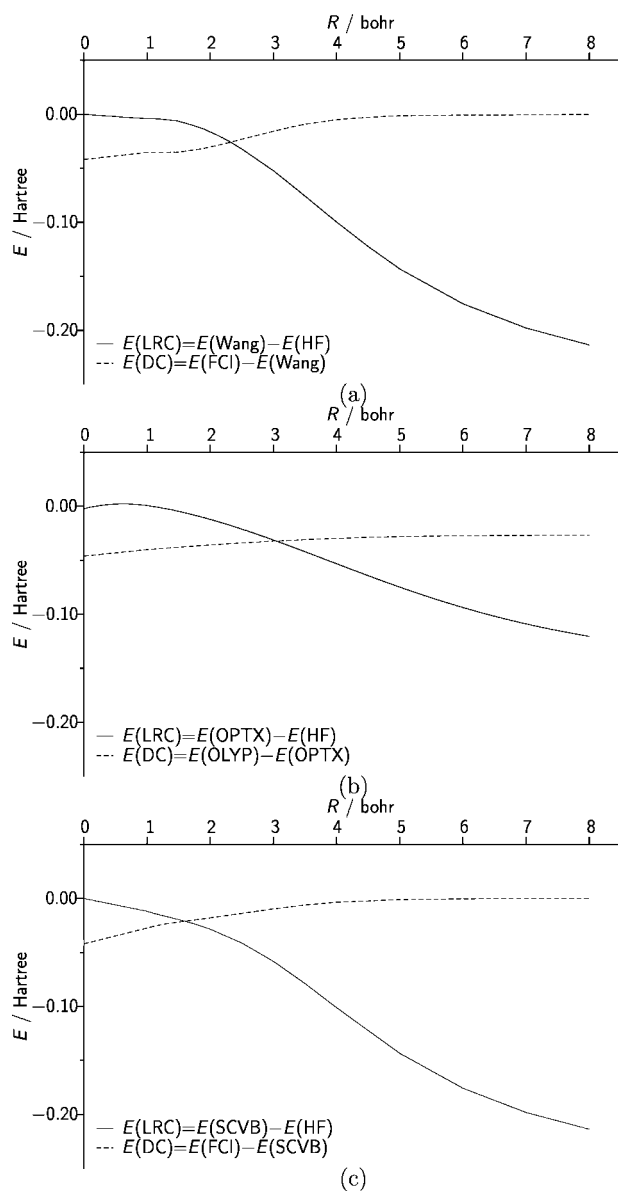


FIGURE 2. Left-right $E(\text{LRC})$ and dynamic $E(\text{DC})$ correlation energies, calculated by (a) QC(Wang, FCI), (b) DFT (OPTX, OLYP), and (c) QC(SCVB, FCI).

The two plots are rather similar at equilibrium, but differ at other distances. The LRC provided by OPTX is entirely insufficient at long-range. Notably the LYP correction has similar behaviour to Eq. (16) for short distances. However, asymptotically it approaches an incorrect nonzero value at long-range, due to the presence of both α and β spins in the atomic fragments. The QC and DFT approaches also have $E(\text{LRC}) = E(\text{DC})$ at different bond lengths—2.3 and 3.1 bohr, respectively.

2.2. THE SPIN-COUPLED VB WAVEFUNCTION

The energy from the s-based Wang approach can be lowered by introducing higher angular momentum functions. Such calculations are known as spin-coupled valence bond (SCVB), introduced by Wilson and Gerratt [24]. They used a $1s, 2s, 2p\sigma, 3d\sigma$ basis. The PE curve is included with HF and FCI in Figure 3. The SCVB bondlength is $1.429a_0$, and the binding energy is 4.13 eV.

If we now define the LRX approach in Eq. (5) to be SCVB, then the correlation components become

$$E(\text{LRC}) = E(\text{SCVB}) - E(\text{HF}) \quad (19)$$

$$E(\text{DC}) = E(\text{FCI}) - E(\text{SCVB}) \quad (20)$$

which are plotted in Figure 2(c). At the united atom the value of $E(\text{DC})$ is known to be $-0.042 E_h$, and for greater than $6 a_0$, it is very close to zero. At equilibrium ($1.4 a_0$), from the SCVB calculations $E(\text{DC})$ is calculated to be $-0.022 E_h$ and so the $E(\text{LRC})$ must be $-0.019 E_h$ (because the total correlation energy is $-0.041 E_h$). In other words at molecular equilibrium, the $E(\text{LRC})$ and $E(\text{DC})$ have almost the same value. We see that $E(\text{LRC}) = E(\text{DC})$ at 1.6 bohr for SCVB; this point is at longer bond lengths with both the Wang and OPTX methods.

It is clear from Figure 2 that the LRC and DC defined using OPTX are much closer to those determined using the Wang QC method, than SCVB. The higher angular momentum functions have a significant effect in the latter approach. It does not seem to be generally appreciated that, based on SCVB, there is a significant reduction in the value of DC at equilibrium.

2.3. CONSEQUENCES FOR DFT

We can envisage a Kohn–Sham calculation based on HL wavefunctions. Wilson and Gerratt [24] have

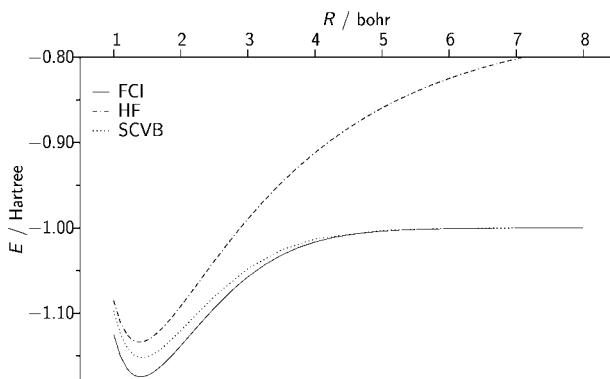


FIGURE 3. Potential energy curves for H_2 calculated by the QC methodologies HF, FCI, SCVB.

derived the self consistent equations (and therefore the appropriate operator) for SCVB wavefunctions. To this operator should be added the potential of an appropriate DC functional. These are DFT-like equations which use only the dynamic correlation functional. Unfortunately the operator for HL is non-trivial due to nonorthogonality problems, so it is unlikely that such calculations will occur in the near future, but they have the advantage that exchange effects which are dominant are dealt with by QM, and DC effects which are more straightforward, are treated by DFT. For existing DC functionals, the s-optimized Wang approach is preferable to SCVB.

Another prospect is the development of both exchange and correlation functionals that accurately describe the dissociation process. Using for instance the Wang definition for the LRC energy, points along the dissociation path could be included in the derivation of a functional, as opposed to the standard approach which involves only atoms and molecules near equilibrium. It also highlights that for some definitions the value of LRC may not be insignificant, even at molecular equilibrium.

Corongiu and Clementi [25] have recently presented a detailed summary of their work on the HF and HL methodologies, and the linear combination HF-HL. Their work is relevant to this article for example they define the correlation energy for the HL wavefunction as $E_c = E_{\text{exact}} - E_{\text{HL}}$, and they give a value of -0.0242 hartrees for H_2 [this is close to our $E(\text{DC})$ for SCVB]. Notably they ascribe near-degeneracy effects to non-dynamical correlation. This is at variance with our work (see our discussion on Be). We do not think their linear combination method HF-HL is related to any DFT functional as the introduction of a linear combination coefficient precludes this. On the other hand they suggest using a correlation functional as an 'add-on' to their HF-HL methods, in the same way as we suggest using a dynamical correlation functional as an add-on.

3. Summary and Conclusion

In this brief article, we have considered the nature of exchange, dynamic correlation (DC) and left-right correlation (LRC) in DFT and wavefunction-based quantum chemistry. We have highlighted the presence of LRC in approximate DFT exchange functionals and considered the separation of LRC and DC in molecular systems. We then argued that

the Heitler–London approach in H_2 includes the essential elements of exchange and LRC. Support for these arguments was provided by a comparison of s-optimised Heitler–London and OPTX potential energy curves in H_2 . The curves agree well near equilibrium, but differ at larger distances, due to the OPTX form. LRC and DC values determined using the two approaches have been compared. The influence of higher angular momentum functions in the Wang Heitler–London approach (SCVB) was then considered; the agreement with OPTX degrades, leading to rather different definitions of LRC and DC. For existing DC functionals, the Wang Heitler–London wavefunction represents the most promising definition of LRC.

The work also highlights several deficiencies of existing exchange–correlation functionals in describing dissociation processes, illustrated with the example of H_2 . We believe that the definitions here (particularly the Wang Heitler–London wavefunction) may aid the development of functionals able to describe molecular dissociation.

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