

Density Functional Theory

Density functional theory is an approach to studying the Schrödinger equation by writing quantities of interest, such as energies, in terms of the particle density, instead of in terms of the wave function. This can simplify computations considerably, especially when the number of particles is large.

To be more specific, consider an N -electron system, with Hamiltonian given by

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V},$$

where

$$\hat{T} = -\frac{1}{2} \sum_{j=1}^N \nabla_j^2, \quad \hat{V}_{ee} = \sum_{1 \leq i < j \leq N} \frac{1}{|\vec{r}_i - \vec{r}_j|}, \quad \hat{V} = \sum_{i=1}^N v(\vec{r}_i) = \sum_{i=1}^N \int d^3r \delta(\vec{r} - \vec{r}_i) v(\vec{r}),$$

and where v is the potential coming from the external forces on the electrons. Here \hat{T} is the kinetic energy term, \hat{V}_{ee} is the repulsive Coulomb potential energy between the electrons, and \hat{V} is the potential energy due to external forces. We are using atomic units: this means Planck's constant \hbar , the electron mass m_e , and the magnitude of the electron charge e are all equal to 1. The unit of distance is the Bohr radius $a_0 = \hbar^2/(me^2)$, and the unit of energy is the hartree $\epsilon_0 = e^2/a_0$. One Bohr radius is about $5.29 \cdot 10^{-11}$ meters and one hartree is about 27.2 electron volts. We are ignoring the sizes of the nuclei, the movements of the nuclei, spin, and relativistic effects.

For example, consider a system of N electrons in a molecule made up of M atoms. Then v is the attractive Coulomb potential energy arising from the M atomic nuclei, given by

$$v(\vec{r}) = \sum_{k=1}^M \frac{-Z_k}{|\vec{r} - \vec{R}_k|}, \tag{1}$$

where \vec{R}_k is the position of the k th nucleus and Z_k is the number of protons it has.

The density is defined by

$$n(\vec{r}) = \langle \psi | \hat{n}(\vec{r}) | \psi \rangle = \int d^3r_1 \int d^3r_2 \cdots \int d^3r_N \psi^*(\vec{r}_1, \dots, \vec{r}_N) \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \psi(\vec{r}_1, \dots, \vec{r}_N).$$

Note that, for any region U , the quantity $\int_U d^3r n(\vec{r})$ gives the expected value of the number of electrons to be found in U .

The basic case is the hydrogen atom, where $N = M = Z_1 = 1$. The ground state energy of the electron is precisely -0.5 Hartrees, the corresponding wavefunction is $\psi(r) = e^{-r}/\sqrt{\pi}$, the density is $n(r) = e^{-2r}/\pi$, and the probability density of the electron being at distance r from the nucleus is $4\pi r^2 n(r)$ and it achieves its maximum at precisely $r = 1$ Bohr radius.

The point of density functional theory is, instead of writing and computing in terms of ψ , to write and compute in terms of n . The basic result is the Hohenberg–Kohn Theorem [HoKo], which says that if $n(\vec{r})$ is a ground state density, then no information is lost by doing this.

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Hohenberg–Kohn Theorem. Consider two N -electron systems, with Hamiltonians \hat{H}_1 and \hat{H}_2 defined by:

$$\hat{H}_k = \hat{T} + \hat{V}_{ee} + \hat{V}_k,$$

with

$$\hat{V}_k = \sum_{i=1}^N v_k(\vec{r}_i) = \sum_{i=1}^N \int d^3r \delta(\vec{r} - \vec{r}_i) v_k(\vec{r}),$$

and where each v_k is continuous except perhaps at some isolated points where it may go to infinity (the nuclei).

THEOREM. Suppose each Hamiltonian \hat{H}_k has at least one normalizable ground state $|\psi_k\rangle$, and these ground states lead to identical densities

$$n(\vec{r}) = \langle \psi_1 | \hat{n}(\vec{r}) | \psi_1 \rangle = \langle \psi_2 | \hat{n}(\vec{r}) | \psi_2 \rangle,$$

where

$$\langle \psi_k | \hat{n}(\vec{r}) | \psi_k \rangle = \int d^3r_1 \int d^3r_2 \cdots \int d^3r_N \psi_k^*(\vec{r}_1, \dots, \vec{r}_N) \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \psi_k(\vec{r}_1, \dots, \vec{r}_N).$$

Then $v_1 - v_2$ is a constant.

Proof. By the variational principle,

$$\langle \psi_1 | \hat{H}_1 | \psi_1 \rangle \leq \langle \psi_2 | \hat{H}_1 | \psi_2 \rangle. \quad (2)$$

Since

$$\begin{aligned} \langle \psi_k | \hat{V}_1 | \psi_k \rangle &= \int d^3r_1 \int d^3r_2 \cdots \int d^3r_N \psi_k^*(\vec{r}_1, \dots, \vec{r}_N) \sum_{i=1}^N \int d^3r \delta(\vec{r} - \vec{r}_i) v_1(\vec{r}) \psi_k(\vec{r}_1, \dots, \vec{r}_N) \\ &= \int d^3r v_1(\vec{r}) n(\vec{r}), \end{aligned}$$

and the right hand side is independent of k , (2) simplifies to

$$\langle \psi_1 | \hat{T} + \hat{V}_{ee} | \psi_1 \rangle \leq \langle \psi_2 | \hat{T} + \hat{V}_{ee} | \psi_2 \rangle.$$

In the same way, starting from $\langle \psi_2 | \hat{H}_2 | \psi_2 \rangle \leq \langle \psi_1 | \hat{H}_2 | \psi_1 \rangle$, we get

$$\langle \psi_2 | \hat{T} + \hat{V}_{ee} | \psi_2 \rangle \leq \langle \psi_1 | \hat{T} + \hat{V}_{ee} | \psi_1 \rangle.$$

Hence both sides are equal and it follows that both $|\psi_1\rangle$ and $|\psi_2\rangle$ are ground states of both Hamiltonians. Then the result follows from the Lemma below. \square

LEMMA. If there exists a state $|\psi\rangle$ which is an eigenstate of both Hamiltonians \hat{H}_1 and \hat{H}_2 , then $v_1 - v_2$ is a constant.

Proof. We have

$$\hat{H}_1 |\psi\rangle = E_1 |\psi\rangle \quad \text{and} \quad \hat{H}_2 |\psi\rangle = E_2 |\psi\rangle,$$

for some E_1 and E_2 . Subtracting, we get

$$(\hat{V}_1 - \hat{V}_2 - E_1 + E_2) |\psi\rangle = 0,$$

and hence

$$W(\vec{r}_1, \dots, \vec{r}_N) \psi(\vec{r}_1, \dots, \vec{r}_N) = 0, \quad \text{where} \quad W(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i=1}^N (v_1(\vec{r}_i) - v_2(\vec{r}_i)) - E_1 + E_2. \quad (3)$$

From this we will conclude that $W(\vec{r}_1, \dots, \vec{r}_N) = 0$ for all points $(\vec{r}_1, \dots, \vec{r}_N)$. This will complete the proof because then $\sum_{i=1}^N (v_1(\vec{r}_i) - v_2(\vec{r}_i)) - E_1 + E_2 = 0$ which implies $v_1(\vec{r}_i) - v_2(\vec{r}_i)$ is independent of \vec{r}_i . The tricky part here is that we must rule out the possibility that $\psi = 0$ and $W \neq 0$. We will use the fact (due to quantum tunneling/unique continuation) that $\int_U |\psi|^2 > 0$ for any region U .

To carry this out, multiply (3) by $\psi^*(\vec{r}_1, \dots, \vec{r}_N)$ and integrate over an arbitrary region U to obtain

$$\int_U W |\psi|^2 = 0,$$

for any region U . We have

$$0 = \int_U W |\psi|^2 \leq \max_U W \int_U |\psi|^2,$$

which implies $\max_U W \geq 0$, and similarly

$$0 = \int_U W |\psi|^2 \geq \min_U W \int_U |\psi|^2,$$

which implies $\min_U W \leq 0$. Hence

$$\min_U W \leq 0 \leq \max_U W. \quad (4)$$

Fix any point $(\vec{r}_1, \dots, \vec{r}_N)$, and consider regions U containing that point and getting smaller and smaller. As the diameter of U goes to zero, both $\min_U W$ and $\max_U W$ converge to $W(\vec{r}_1, \dots, \vec{r}_N)$ because W is continuous. Hence, (4) becomes

$$W(\vec{r}_1, \dots, \vec{r}_N) \leq 0 \leq W(\vec{r}_1, \dots, \vec{r}_N),$$

which implies $W(\vec{r}_1, \dots, \vec{r}_N) = 0$. Since the point $(\vec{r}_1, \dots, \vec{r}_N)$ was arbitrary, it follows that $W = 0$ everywhere. \square

Levy's constrained search. We assume that \hat{H} has a normalizable ground state. Then by the variational principle the energy of this ground state is given by

$$E = \min_{\psi} \langle \psi | \hat{H} | \psi \rangle,$$

where the minimum is taken over normalized antisymmetric states ψ with finite kinetic energy.¹

Following Levy [Lev], we write this as

$$E = \min_n E[n], \quad \text{with} \quad E[n] = F[n] + V[n],$$

$$F[n] = \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle, \quad V[n] = \langle \psi | \hat{V} | \psi \rangle = \int d^3 \vec{r} v(\vec{r}) n(\vec{r}),$$

where the \min_n is taken over normalized nonnegative densities n with finite kinetic energy and the $\min_{\psi \rightarrow n}$ is taken over normalized states ψ with $\langle \psi | \hat{n}(\vec{r}) | \psi \rangle = n(\vec{r})$.²

¹The antisymmetry condition is that, if $1 \leq i < k \leq N$, then $\psi(\vec{r}_1, \dots, \vec{r}_{i-1}, \vec{r}_i, \vec{r}_{i+1}, \dots, \vec{r}_{k-1}, \vec{r}_k, \vec{r}_{k+1}, \dots, \vec{r}_N) = -\psi(\vec{r}_1, \dots, \vec{r}_{i-1}, \vec{r}_k, \vec{r}_{i+1}, \dots, \vec{r}_{k-1}, \vec{r}_i, \vec{r}_{k+1}, \dots, \vec{r}_N)$. The normalization condition is $\langle \psi | \psi \rangle = 1$. The finite kinetic energy condition is that $\langle \psi | \hat{T} | \psi \rangle$ is finite. For v given by attractive Coulomb forces as in equation (1) above, it follows that $\langle \psi | \hat{H} | \psi \rangle$ is finite as well; see the Technical Remark between equations (3.6) and (3.7) of [Lie] for more.

²The nonnegativity condition is that $n(\vec{r}) \geq 0$ for all \vec{r} . The normalization is that $\int d^3 r n(\vec{r}) = N$. The finite kinetic energy condition is that $\int d^3 r (\nabla \sqrt{n(\vec{r})})^2$ is finite. One can show that if ψ is as in the previous footnote, then $n(\vec{r}) = \langle \psi | \hat{n}(\vec{r}) | \psi \rangle$ has these properties. Conversely, given n with these properties, one can find ψ as in the previous footnote (having the form of a Slater determinant) such that $n(\vec{r}) = \langle \psi | \hat{n}(\vec{r}) | \psi \rangle$. See Theorems 1.1 and 1.2 of [Lie] for more, and see also [Har].

By the method of Lagrange multipliers, solutions to this constrained minimization problem will be critical points of the Lagrangian $E[n] - \mu N[n]$, where $N[n] = \int d^3r n(\vec{r})$, i.e. they are solutions to the Euler–Lagrange equation

$$\frac{\delta E[n]}{\delta n} - \mu \frac{\delta N[n]}{\delta n} = 0, \quad \text{or} \quad \frac{\delta F[n]}{\delta n} + v(\vec{r}) - \mu = 0, \quad (5)$$

where the Lagrange multiplier constant μ is determined by requiring that the solution obey the constraint $N[n] = \int d^3r n(\vec{r}) = N$.³

Because $F[n]$ is so complicated, we look for a good approximation which is simpler. The first one comes from Thomas [Tho] and Fermi’s [Fer] calculations treating the electron cloud as homogeneous and unbounded.

Thomas–Fermi approximation. In this approximation we replace $F[n]$ by

$$F^{TF}[n] = T_s^{TF}[n] + E_H[n], \quad (6)$$

where

$$T_s^{TF}[n] = A_s \int d^3r n^{5/3}(\vec{r}), \quad E_H[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}, \quad A_s = \frac{3}{10}(3\pi^2)^{2/3}. \quad (7)$$

Here $T_s^{TF}[n]$ approximates the kinetic energy $\langle \psi | \hat{T} | \psi \rangle$, and $E_H[n]$, called the *Hartree energy*, approximates the interaction energy $\langle \psi | \hat{V}_{ee} | \psi \rangle$. The formula for $T_s^{TF}[n]$ comes from treating the electrons as noninteracting particles in a large box [GrSc, Equation (5.56)]. The formula for $E_H[n]$ comes from electrostatics, where by Coulomb’s law $E_H[n]$ is the energy of the charge distribution $n(\vec{r})$ [Gri, Equations (2.43) and (2.29)]. Differentiating (6) gives

$$\frac{\delta F^{TF}[n]}{\delta n} = \frac{5}{3} A_s n^{2/3}(\vec{r}) + \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}.$$

If we neglect interactions, (i.e. delete the Hartree term) then the Euler–Lagrange equation (5) becomes

$$\frac{5}{3} A_s n^{2/3}(\vec{r}) + v(\vec{r}) = \mu, \quad \implies \quad n(\vec{r}) = \left[\frac{3}{5A_s} (\mu - v(\vec{r})) \right]^{3/2}.$$

Unfortunately this is a complex number if $\mu - v(\vec{r}) < 0$, so we use instead $n(\vec{r}) = \left[\frac{3}{5A_s} (\mu - v(\vec{r})) \right]^{3/2}$ only when $\mu > v(\vec{r})$ and set $n(\vec{r}) = 0$ when $\mu \leq v(\vec{r})$. Notice that μ has units of energy, and if we interpret it as the highest occupied energy of the electrons then the region where we have set $n(\vec{r}) = 0$ is precisely the classically forbidden region.

Kohn–Sham method. The Kohn–Sham method [KoSh] computes densities and energies using a fictitious N -particle non-interacting system, designed so that its ground state density is the same as the ground state density for the N -particle interacting system \hat{H} .

More precisely, let $v_s(\vec{r})$ be the potential (called the *Kohn–Sham potential*) such that if $\epsilon_1, \dots, \epsilon_N$ are the N lowest energies and $\varphi_1, \dots, \varphi_N$ corresponding normalized states (called *Kohn–Sham orbitals*) for the single particle problem

$$\left(-\frac{1}{2} \nabla^2 + v_s(\vec{r}) \right) \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r}),$$

³Is there a way to check if a given solution to this equation is the right one? Might we end up at a critical point of E which is not the minimum?

then

$$n(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2,$$

where this n is the same as the one for the ground state of the problem we are studying. By the Hohenberg–Kohn theorem, this requirement determines the potential up to an overall constant. This constant is chosen so that the corresponding Euler–Lagrange equations have the same Lagrange multiplier constant μ as the one from (5). More precisely, the Kohn–Sham system has energy functional

$$E_s[n] = T_s[n] + \int d^3r v_s(\vec{r})n(\vec{r}),$$

with kinetic energy given by

$$T_s[n] = \frac{1}{2} \sum_{i=1}^N \int d^3r |\vec{\nabla} \varphi_i(\vec{r})|^2, \quad (8)$$

and so its Euler–Lagrange equation is

$$\frac{\delta T_s[n]}{\delta n} + v_s(\vec{r}) - \mu = 0, \quad (9)$$

where the constant μ is determined by requiring that the solution obey $\int d^3r n(\vec{r}) = N$. The Kohn–Sham potential v_s is chosen such that the Lagrange multiplier constant μ appearing in (9) is the same as the original one from (5).

We now proceed to expand the complicated energy functional $F[n]$ in the following way:

$$F[n] = T_s[n] + E_H[n] + E_x[n] + E_c[n].$$

Typically we have $T_s[n] \gg E_H[n] \gg -E_x[n] \gg -E_c[n] > 0$; see [Bur, Table 7.1] for some example values (note that E_H is denoted U there, and that one writes $E_{xc} = E_c + E_x$, $T_c = T - T_s$). Here the Kohn–Sham kinetic energy $T_s[n]$ and the Hartree energy $E_H[n]$ have already been defined in (8) and (7) respectively. The *exchange energy* E_x is defined by

$$E_x[n] = \langle \Phi | \hat{V}_{ee} | \Phi \rangle - E_H[n],$$

and the *correlation energy* E_c is defined by

$$E_c[n] = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle - \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle,$$

where Φ is defined by the Slater determinant

$$\Phi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \det[\varphi_j(\vec{r}_k)],$$

and we are taking the determinant of the matrix whose entry in the j th row and k th column is $\varphi_j(\vec{r}_k)$. Thus Φ is the ground state wave function of the N -particle Kohn–Sham system. The density and Kohn–Sham kinetic energy are given in terms of Φ by

$$n(\vec{r}) = \langle \Phi | \hat{n}(\vec{r}) | \Phi \rangle, \quad T_s[n] = \langle \Phi | \hat{T} | \Phi \rangle,$$

and Φ has the following minimization property:

$$\langle \Phi | \hat{T} | \Phi \rangle \leq \langle \tilde{\Phi} | \hat{T} | \tilde{\Phi} \rangle,$$

where $\tilde{\Phi}$ is any Slater determinant obeying $n(\vec{r}) = \langle \tilde{\Phi} | \hat{n}(\vec{r}) | \tilde{\Phi} \rangle$.

The exchange energy also obeys the formula

$$E_x[n] = -\frac{1}{2} \int d^3r \int d^3r' \sum_{j \neq k=1}^N \frac{\varphi_j^*(\vec{r}) \varphi_k^*(\vec{r}') \varphi_k(\vec{r}) \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|}.$$

The Kohn–Sham potential is given by⁴

$$v_s = v + v_H + v_{xc},$$

where

$$v_H(\vec{r}) = \frac{\delta E_H[n]}{\delta n} = \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}, \quad v_{xc}(\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n}.$$

Kohn–Sham algorithm. In computations, one typically uses the Kohn–Sham method to approximate a ground state density and energy using the following steps:

- (1) Choose an explicit approximation for the implicitly defined exchange correlation energy, $E_{xc}^{\approx}[n] \approx E_{xc}[n]$.
- (2) Choose a starting density $n(\vec{r})$ which is as close as possible to the true ground state density, and compute the corresponding approximate Kohn–Sham potential

$$v_s^{\approx} = v + v_H + v_{xc}^{\approx}, \quad v_{xc}^{\approx}(\vec{r}) = \frac{\delta E_{xc}^{\approx}[n]}{\delta n}.$$

- (3) Find the N -particle ground state Φ of the corresponding Kohn–Sham system

$$\left(-\frac{1}{2} \nabla^2 + v_s^{\approx}(\vec{r}) \right) \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r}),$$

and use it to compute a new density $n(\vec{r}) = \langle \Phi | \hat{n}(\vec{r}) | \Phi \rangle = \sum_{i=1}^N |\varphi_i(\vec{r})|^2$.

- (4) Redo step (2) with the previous input density n replaced by the new output density from step (3).
- (5) Iterate this process to get a sequence of densities n_1, n_2, n_3, \dots which hopefully converges.
- (6) To get the ground state energy, plug the limiting density, or a later term in the sequence, into

$$E^{\approx}[n] = T_s[n] + E_H[n] + E_{xc}^{\approx}[n].$$

As a basic choice one may take $E_{xc}^{\approx}[n] = 0$. This is called the *Hartree approximation*. It typically leads to bond lengths that are too large by 10 to 20%, and atoms barely binding to form molecules and solids.

A more accurate approximation is the Local Density Approximation (LDA), described below.

Local Density Approximation. This way of approximating the exchange correlation energy was introduced in [KoSh]. One takes $E_{xc}^{\approx} = E_{xc}^{LDA}$, where

$$E_{xc}^{LDA}[n] = \int d^3r n(\vec{r}) \epsilon_{xc}^{unif}(n(\vec{r})),$$

where ϵ_{xc}^{unif} is the exchange correlation energy per particle of an interacting electron gas of uniform density n . In other words, we locally approximate the true density by a constant density. By construction, ϵ_{xc}^{unif} is exact for a uniform density, and it is more accurate when the density is more slowly varying. To compute it, we consider separately the exchange and correlation contributions, and write $\epsilon_{xc}^{unif} = \epsilon_x^{unif} + \epsilon_c^{unif}$.

⁴Is it easy to see that no constant needs to be added here? See [KoSh, Equation (2.8)]?

From Thomas–Fermi theory, the exchange contribution is $\epsilon_x^{unif}(n) = \frac{3}{4\pi}(3\pi^2n)^{1/3}$.

The correlation contribution is much more complicated. Wigner in the 1930s approximated it as $\epsilon_c^{unif}(n) \approx \frac{-a}{b+r_s}$, where $r_s = (\frac{4\pi n}{3})^{-1/3}$ is the radius of the sphere having volume $1/n$, and where a and b are positive numbers obtained from numerical studies of the $n \rightarrow \infty$ and $n \rightarrow 0$ limits. Close approximations are also more complicated. An accurate formula was obtained by Perdew and Wang in 1992 [PeWa].

Such approximations leads to bond lengths that are too small by a few percent, and binding energies that are too large by about 10%.

Constraints on functionals. As we look for better approximations than the local density approximation, we bear in mind certain constraints satisfied by the true functionals.

One constraint is derived from the *uniform coordinate scaling*. For any $\gamma > 0$ and any state ψ , we put

$$\psi_\gamma(\mathbf{r}) = \gamma^{3N/2}\psi(\gamma\mathbf{r}),$$

where $\mathbf{r} = (\vec{r}_1, \dots, \vec{r}_N)$. This scaling preserves normalization: if $\langle \psi | \psi \rangle = \int d^3N\mathbf{r} |\psi(\mathbf{r})|^2 = 1$, then

$$\int d^3N\mathbf{r} |\psi_\gamma(\mathbf{r})|^2 = \gamma^{3N} \int d^3N\mathbf{r} |\psi(\gamma\mathbf{r})|^2 = \int d^3N\mathbf{r} |\psi(\mathbf{r})|^2 = 1.$$

Similar calculations show that

$$\langle \psi_\gamma | \hat{T} | \psi_\gamma \rangle = \gamma^2 \langle \psi | \hat{T} | \psi \rangle, \quad \langle \psi_\gamma | \hat{V}_{ee} | \psi_\gamma \rangle = \gamma \langle \psi | \hat{V}_{ee} | \psi \rangle,$$

and, using $n_\gamma(\vec{r}) = \gamma^3 n(\gamma\vec{r})$ for the density corresponding to ψ_γ ,

$$E_H[n_\gamma] = \gamma E_H[n]$$

One can also show that E_x obeys the same scaling. Note that for the local density approximation we have the scaling

$$\epsilon_x^{unif}(\gamma^3 n(\vec{r})) = \gamma \epsilon_x^{unif}(n(\vec{r})).$$

which implies

$$E_x^{LDA}[n_\gamma] = \gamma^3 \int d^3r n(\gamma\vec{r}) \epsilon_x^{unif}(\gamma^3 n(\gamma\vec{r})) = \int d^3r n(\vec{r}) \epsilon_x^{unif}(\gamma^3 n(\vec{r})) = \gamma E_x^{LDA}[n].$$

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