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Current density functional theory for optical spectra: A polarization functional

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In this paper we present a new approach to calculate optical spectra, which for the first time uses a polarization dependent functional within current density functional theory (CDFT), which was proposed by Vignale and Kohn [Phys. Rev. Lett. **77**, 2037 (1996)]. This polarization dependent functional includes exchange-correlation (xc) contributions in the effective macroscopic electric field. This functional is used to calculate the optical absorption spectrum of several common semiconductors. We achieved in all cases good agreement with experiment. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1385370]

I. INTRODUCTION

Time-dependent density functional theory (TDDFT), as formulated by Runge and Gross,[1] makes it *in principle* possible to study the dynamical properties of interacting many-particle systems. The formulation of a local *dynamical* approximation for the xc potential turns out to be extremely difficult, because such an xc potential in TDDFT is an intrinsically nonlocal functional of the density (i.e., there does not exist a gradient expansion for the frequency-dependent xc potential in terms of the density alone). Vignale and Kohn[2] were the first who formulated a local gradient expansion in terms of the *current density*. In a time-dependent current density functional approach to linear response theory, they derived an expression for the linearized xc vector potential $\mathbf{a}_{xc}(\mathbf{r}, \omega)$ for a system of slowly varying density, subject to a spatially slowly varying external potential at a finite frequency ω.

II. THEORY

Let us first recall our definitions for the macroscopic electric field and polarization, before we derive an expression in which the macroscopic xc potential contributions of Vignale and Kohn[2] are incorporated. If we apply a time-dependent electric field of frequency ω, we will induce a macroscopic polarization $\mathbf{P}_{mac}(\omega)$ which will be proportional to the macroscopic field $\mathbf{E}_{mac}(\omega)$, i.e., the applied field plus the average electric field caused by induced charges in the solid. The constant of proportionality is known as the electric susceptibility and is a material property,

$$\mathbf{P}_{mac}(\omega) = \chi(\omega) \cdot \mathbf{E}_{mac}(\omega). \tag{1}$$

The macroscopic polarization is defined by the induced current density,

$$\mathbf{P}_{mac}(\omega) = \frac{i}{\omega V} \int_V \delta\mathbf{j}(\mathbf{r}, \omega) d\mathbf{r}. \tag{2}$$

We see that if we want to calculate the susceptibility and the related dielectric function we need to calculate the induced current. The induced current $\delta\mathbf{j}$ and induced density $\delta\rho$ can, in principle, be calculated from the current–current and density–current response functions of the solid in the following way, where we use a shortened notation which implies integration over spatial coordinates:[3]

$$\delta\mathbf{j} = \frac{i}{\omega} \chi_{\mathbf{j}\mathbf{j}} \cdot \mathbf{E}_{mac}, \tag{3}$$

$$\delta\rho = \frac{i}{\omega} \chi_{\rho\mathbf{j}} \cdot \mathbf{E}_{mac}. \tag{4}$$

This requires, however, knowledge of the exact response functions of the system. Within a Kohn–Sham formulation the exact density and current response are calculated as the response of an auxiliary noninteracting system to an effective electric field and potential,

$$\delta\mathbf{j} = \frac{i}{\omega} \chi_{\mathbf{j}\mathbf{j}}^s \cdot \mathbf{E}_{eff} + \chi_{\mathbf{j}\rho}^s \delta v_{eff}, \tag{5}$$

$$\delta\rho = \frac{i}{\omega} \chi_{\rho\mathbf{j}}^s \cdot \mathbf{E}_{eff} + \chi_{\rho\rho}^s \delta v_{eff}, \tag{6}$$

where the superscript s indicates that we are dealing with the response functions of the noninteracting Kohn–Sham system. The equations above are our basic equations of time-dependent current-density functional theory (TDCDFT). The effective fields have the property that they produce the exact density and current when applied to the Kohn–Sham system. Hence they are functionals of $\delta\rho$ and $\delta\mathbf{j}$, and have to be obtained self-consistently. If we neglect the microscopic contributions to the transverse components, we can split up these fields as follows:

$$\mathbf{E}_{eff}(\omega) = \mathbf{E}_{mac}(\omega) + \mathbf{E}_{xc,mac}(\omega), \tag{7}$$

$$\delta v_{eff}(\mathbf{r}, \omega) = \delta v_{mic}(\mathbf{r}, \omega) + \delta v_{xc,mic}(\mathbf{r}, \omega), \tag{8}$$

where v_{mic} is the microscopic part of the Hartree potential and $v_{xc,mic}$ is the microscopic part of the exchange-correlation potential. The term $\mathbf{E}_{xc,mac}$ denotes the macroscopic xc-electric field. The gauge is chosen in such a way

that the microscopic parts of the external field are included in the scalar potential and the macroscopic part of the fields are included in the vector potential. Our goal is to derive an expression for $\mathbf{E}_{xc,mac}$. Let us first look at the consequences of such a term. With Kohn–Sham theory the macroscopic polarizability is proportional to the effective field $\mathbf{E}_{eff}$. This defines a Kohn–Sham susceptibility $\widetilde{\chi}$ by the equation,

$$\mathbf{P}_{mac}(\omega) = \widetilde{\chi}(\omega) \cdot \mathbf{E}_{eff}(\omega). \tag{9}$$

We are, however, interested in the actual susceptibility χ. With Eqs. (1), (7), and (9) we obtain

$$(\widetilde{\chi}^{-1}(\omega) - \chi^{-1}(\omega)) \cdot \mathbf{P}_{mac}(\omega) = \mathbf{E}_{xc,mac}(\omega). \tag{10}$$

We see that we can calculate the susceptibility χ once we know how to calculate $\mathbf{E}_{xc,mac}$. In previous calculations,[3,4] $\mathbf{E}_{xc,mac}$ was simply put to zero, which yields the approximation $\chi = \widetilde{\chi}$. Here we want to improve upon this approximation and derive an explicit expression for $\mathbf{E}_{xc,mac}$. The starting point is the current–density functional derived by Vignale and Kohn[2,5] which we write in the compact form derived by Vignale, Ullrich and Conti $[\mathbf{E}_{xc1}(\mathbf{r},\omega) \equiv (i\omega/c)\,\mathbf{a}_{xc}(\mathbf{r},\omega)]$,[6]

$$-E_{xc1,i}(\mathbf{r},\omega) = -\partial_i v_{xc1}^{ALDA} + \frac{1}{\rho_0(\mathbf{r})} \sum_j \partial_j \sigma_{xc,ij}(\mathbf{r},\omega). \tag{11}$$

Here $E_{xc1,i}$ is the induced xc-electric field in linear response and v_{xc1}^{ALDA} is the first order change in the xc-potential in the adiabatic local density approximation (ALDA). The last term contains the ground state density ρ_0 of the system and the viscoelastic stress tensor,

$$\sigma_{xc,ij} = \widetilde{\eta}_{xc}\left(\partial_j u_i + \partial_i u_j - \frac{2}{3}\delta_{ij}\left(\sum_k \partial_k u_k\right)\right)$$
$$+ \widetilde{\zeta}_{xc}\delta_{ij}\left(\sum_k \partial_k u_k\right). \tag{12}$$

Here $\mathbf{u}(\mathbf{r},\omega) = \delta\mathbf{j}(\mathbf{r},\omega)/\rho_0(\mathbf{r})$ is the induced velocity field and the constants $\widetilde{\eta}_{xc}(\rho_0,\omega)$ and $\widetilde{\zeta}_{xc}(\rho_0,\omega)$ are coefficients, which can be expressed in terms of the transverse and longitudinal xc-kernels of the electron gas.[6] In order to isolate the macroscopic component of the xc-electric field we take the average over a unit cell of the solid and obtain

$$\mathbf{E}_{xc,mac}(\omega) = \frac{i}{\omega}\sum_k \frac{1}{\Omega}\int_\Omega d\mathbf{r}\, y_{ik}(\mathbf{r},\omega)\,\delta j_k(\mathbf{r},\omega), \tag{13}$$

where Ω denotes the unit cell volume and we defined the matrix,

$$y_{ik}(\mathbf{r},\omega) = -\delta_{ik}\frac{\nabla \cdot (f_{xcT}\nabla\rho_0)}{\rho_0} - \frac{\partial_k(h_{xc}\partial_i\rho_0)}{\rho_0}. \tag{14}$$

Here $f_{xcT}(\rho_0,\omega)$ is the transverse xc-kernel of the electron gas and $h_{xc}(\rho_0,\omega)$ is given as

$$h_{xc}(\rho_0,\omega) = f_{xcL}(\rho_0,\omega) - f_{xcT}(\rho_0,\omega) - \frac{d^2 e_{xc}}{d\rho_0^2}. \tag{15}$$

TABLE I. The calculated values for $\mathbf{Y}([\rho_0],0)$, and the applied energy shifts to the dielectric functions, for the crystals in Figs. 1–5.

| Solid | $\mathbf{Y}([\rho_0],0)$ (a.u.) | Applied shift (eV)[a] | |
		Without $\mathbf{Y}([\rho_0],0)$	With $\mathbf{Y}([\rho_0],0)$
C	0.367	0.60	0.70
Si	0.355	0.40	0.58
GaP	0.409	0.50	0.60
GaAs	0.416	0.45	0.50
ZnS	0.489	0.90	0.90

[a]Spectra have been shifted such that the calculated and experimental zero-crossings of ϵ_1 coincide.

Here $f_{xcL}(\rho_0,\omega)$ is the longitudinal part of the electron gas xc-kernel and e_{xc} is the xc-energy per volume unit of the electron gas. The equation for the macroscopic part of the xc-electric field can be simplified if we replace $\delta\mathbf{j}$ by its macroscopic value, i.e., its average over the unit cell. In that case we obtain

$$\mathbf{E}_{xc,mac}(\omega) = \frac{i}{\omega}\mathbf{Y}([\rho_0],\omega) \cdot \delta\mathbf{j}(\omega)$$
$$= \mathbf{Y}([\rho_0],\omega) \cdot \mathbf{P}_{mac}(\omega). \tag{16}$$

Here the tensor $\mathbf{Y}$ is given by

$$\mathbf{Y}([\rho_0],\omega) = \frac{1}{\Omega}\int_\Omega d\mathbf{r}\,\frac{(\nabla\rho_0)^2}{\rho_0^2}f_{xcT}(\rho_0,\omega)$$
$$+ \frac{1}{\Omega}\int_\Omega d\mathbf{r}\frac{\nabla\rho_0 \otimes \nabla\rho_0}{\rho_0^2}h_{xc}(\rho_0,\omega). \tag{17}$$

Equation (16) represents the first explicit example of the often discussed density-polarization functional.[7,8] With this functional and the Eqs. (1), (7), and (9), we see that the susceptibility becomes equal to

$$\chi(\omega) = (1 - \widetilde{\chi}(\omega)\mathbf{Y}([\rho_0],\omega))^{-1}\widetilde{\chi}(\omega). \tag{18}$$

This equation clearly displays the influence of the macroscopic xc-electric field on the susceptibility. It remains to find an appropriate approximation for the functions f_{xcT} and f_{xcL}. These functions have been investigated in detail for the electron gas.[9–12] In these works it has been shown that they are smooth functions of the frequency, except at twice the plasma frequency. For the optical spectra we are, however, interested in much smaller frequencies. In the limit $\omega \to 0$ the function $h_{xc}(\rho_0,\omega)$ becomes equal to $f_{xcT}(\rho_0,0)/3$.[6] In that limit the tensor $\mathbf{Y}([\rho_0],0)$ is completely determined by $f_{xcT}(\rho_0,0)$.

III. CALCULATIONS

We have tested this new functional for silicon as an example of a group IV semiconductor in the diamond structure. We used Eq. (19) (and the values of μ_{xc} in Table I) of Ref. 11, to obtain values for $f_{xcT}(\rho_0,0)$ at arbitrary ρ_0, thereby using a cubic spline interpolation in the range 0–5 for the r_s values, in which we take into account the exactly known small r_s behavior.[12] The macroscopic dielectric function $\epsilon(\omega)$ can be obtained directly from the electric susceptibility
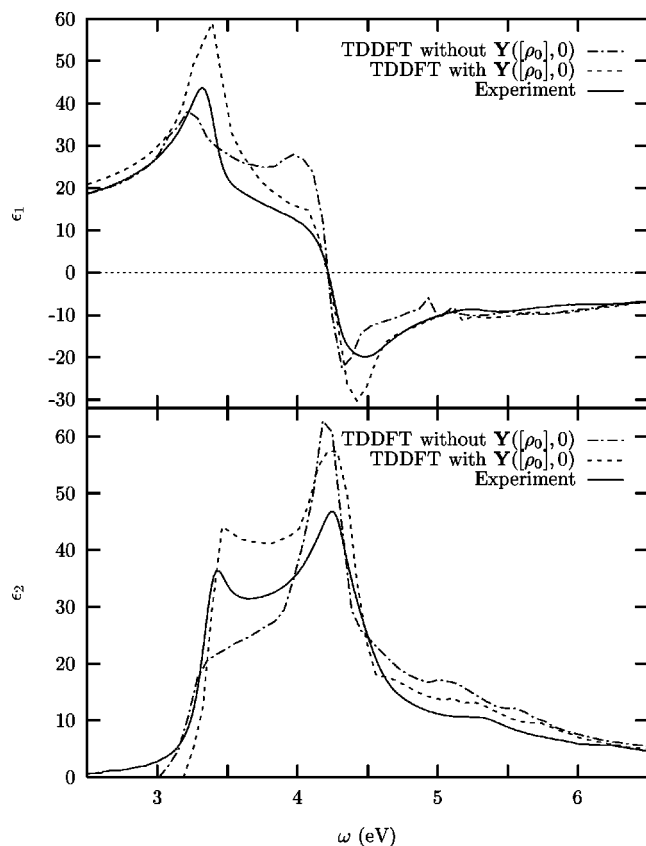
FIG. 1. The dielectric function for silicon (Si), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983); *Handbook of Optical Constants of Solids,* edited by E. D. Palik (Academic, New York, 1985)]. The applied energy shifts to the TDDFT calculated dielectric function were 0.60 eV without, and 0.70 eV with the inclusion of $\mathbf{Y}([\rho_0],0)$.
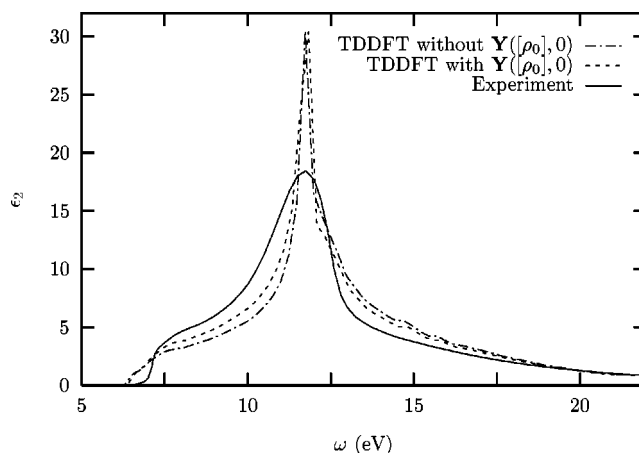

FIG. 2. The optical absorption spectrum for diamond (C), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983)]. The applied energy shifts to the TDDFT calculated dielectric function were 0.40 eV without, and 0.58 eV with the inclusion of $\mathbf{Y}([\rho_0],0)$.

$\chi(\omega)$ through $\epsilon(\omega)=1+4\pi\chi(\omega)$. The optical absorption spectrum ϵ_2 for Si, shows two major peaks in the range from 3–6 eV.[13–16] The first peak (E_1) is attributed to an M_0- or M_1-type critical point transition, and the second (E_2) one to an M_2 type.[17,18] All previous "one-electron" approximations, ranging from the early pseudopotential approaches in the 1970s,[19,20] to the *ab initio* DFT-LDA of the end 1990s,[21] showed the same features for ϵ_2. However, the E_1 peak is usually underestimated, and appears just as a shoulder, whereas the E_2 is overestimated and appears at too high energies compared to experiment.[13,14] The underestimation of the E_1 peak was attributed to excitonic effects (the attractive interaction between the *virtual* hole and the *excited* electron). In the recent calculations,[22] these excitations are explicitly taken into account by solving the Bethe–Salpeter equation (BSE) for the coupled electron–hole excitations, and in these spectra the E_1 peak is clearly resolved and in good agreement with experiment.[13,14] The ratio of the E_1-E_2 peak heights in the ϵ_2 of Si proved to be rather sensitive to the numerical value of $\mathbf{Y}([\rho_0],0)$. However, it turned out that the theoretical value that we list in Table I, is too high by about a factor of 2. In view of the uncertainty in the published values of $f_{xcT}(\rho_0,0)$,[12] we introduce a prefactor of 0.4 in front of the matrix $\mathbf{Y}([\rho_0],0)$ in Eq. (18), which was de-

termined in order to get an optimal agreement with experiment for the ratio of the E_1-E_2 peak heights. This prefactor is used in all the subsequent cases.

IV. RESULTS

A. Silicon

In Fig. 1, we show the effect of this polarization functional on the $\epsilon(\omega)$ of Si in comparison with experiment.[13,14] In order to facilitate the comparison with experiment, the spectra have been shifted to higher energies, see Table I. It is clear that without the $\mathbf{E}_{xc,mac}$ contributions, the E_1 peak appears as a shoulder and is underestimated in amplitude, the E_2 peak is too sharp, and therefore overestimated in magnitude. When including the macroscopic xc-contributions, the E_1 peak is now clearly resolved. As can be seen in Fig. 1, for both the real and imaginary part of $\epsilon(\omega)$, the whole dielectric function is improved considerably. Therefore it should be concluded that it is necessary to include the $\mathbf{E}_{xc,mac}$ contributions to get the E_1 peak in the ϵ_2 of Si in good agreement with experiment.[13,14] In addition, we have calculated the optical absorption spectra ϵ_2 for C, also a group IV element, GaP and GaAs (III–V), and ZnS (II–VI) using the same polarization functional. We checked that the used prefactor led to uniformly improved spectra, and hence we have obtained a new polarization functional that in all cases improves our previous ALDA results.[4]

B. Diamond

The experimental[13] absorption spectrum ϵ_2 for diamond shows an E_2 peak around 12 eV. In all previous calculations of ϵ_2 for C this E_2 peak is overestimated, just like in our recently performed time-dependent DFT calculations,[3,4] as well as in the BSE calculations,[16] which include *in detail* the electron–hole interactions. In Fig. 2 we show the effect of including the polarization functional on the ϵ_2 of diamond, in comparison with experiment.[13] Clearly there is a very small effect on ϵ_2 when using the polarization functional. There-
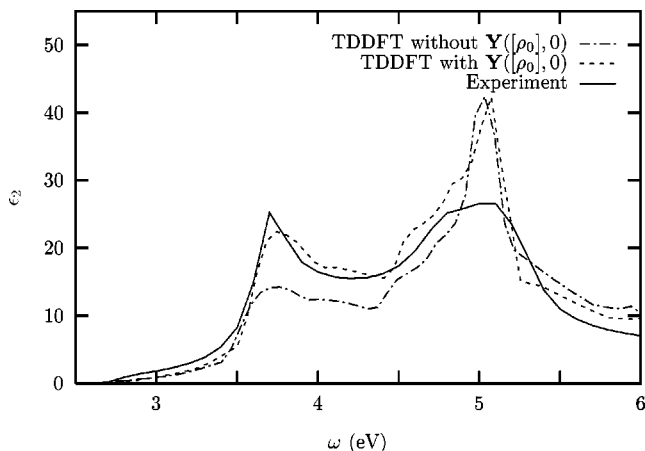
FIG. 3. The optical absorption spectrum for gallium phosphide (GaP), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983)]. The applied energy shifts to the TDDFT calculated dielectric function were 0.50 eV without, and 0.60 eV with the inclusion of $\mathbf{Y}([\rho_0],0)$.

fore it can be concluded that the xc-contributions to the effective macroscopic electric field in diamond are negligible.

C. Gallium phosphide

The experimental[13] absorption spectrum ϵ_2 of GaP in the zincblende structure, also shows a double peak structure in the range from 3 to 6 eV, just like Si. In Fig. 3, the effect of the polarization functional on the ϵ_2 of GaP is shown and compared with experiment.[13] Upon inclusion of the scaled $\mathbf{Y}([\rho_0],0)$ term, the originally underestimated E_1 peak is now found in full agreement with experiment,[13] but the E_2 peak is still overestimated and too sharp.

D. Gallium arsenide

The experimental absorption spectrum for GaAs (Ref. 13) shows the same features as for GaP. In Fig. 4 the effect
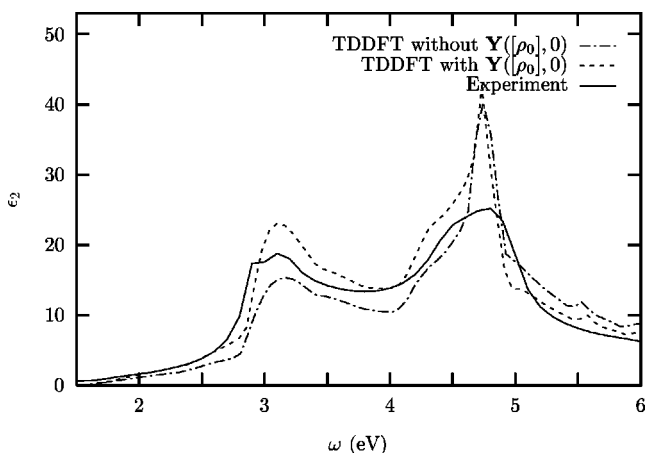

FIG. 4. The optical absorption spectrum for gallium arsenide (GaAs), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983)]. The applied energy shifts to the TDDFT calculated dielectric function were 0.45 eV without, and 0.50 eV with the inclusion of $\mathbf{Y}([\rho_0],0)$.
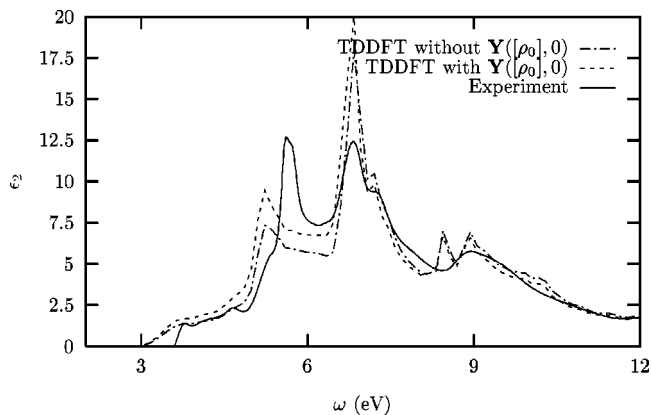

FIG. 5. The optical absorption spectrum for zinc sulfide (ZnS), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [J. L. Freelouf, Phys. Rev. B **7**, 3810 (1973)]. The applied energy shifts to the TDDFT calculated dielectric function were 0.90 eV without and with the inclusion of $\mathbf{Y}([\rho_0],0)$.

of the polarization functional is shown on the ϵ_2 of GaAs. Including $\mathbf{Y}([\rho_0],0)$ gives an increase in the oscillator strength for the E_1 peak, just like in GaP, and it is now also in good agreement with experiment.[13]

E. Zinc sulfide

In the II–VI semiconductor ZnS the E_1 peak is also underestimated in our previous calculations,[4] compared to experiment.[15] In Fig. 5, it can be seen that also for ZnS the oscillator strength for the E_1 peak increases after inclusion of the $\mathbf{Y}([\rho_0],0)$ term, and is now in better agreement with experiment.[15]

V. CONCLUSIONS

In conclusion, we presented the first successful computational approach of a polarization dependent functional within current density functional theory, as it was suggested in 1996 by Vignale and Kohn.[2] The calculated optical absorption spectra of several semiconductors clearly improved considerably with the inclusion of the exchange-correlation contributions to the effective macroscopic electric field.

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