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Dispersion relations in a planar array of alternating organic and inorganic quantum wires

Nguyen Ba An [1]

International Center for Theoretical Physics, P.O. Box 586, 34100 Trieste, Italy

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Abstract

Eigenmode dispersion relations are exactly derived in a planar array of alternating organic and inorganic quantum wires with global interwire interactions taken into account. The obtained eigenmodes differ strongly from the bare excitons and the hybrid excitons. Their dispersions are also qualitatively distinct for different orientations of the exciton dipole moments and expected to greatly modify the optical responses as compared to a conventional array of inorganic semiconducting quantum wires.

Following the successful fabrication of inorganic quantum heterostructures [1] a novel technique of organic molecular beam deposition has recently made also available new kinds of organic heterostructures [2–6]. These are unusual multiple quantum well structures consisting of two incommensurate organic materials 3,4,9,10-perylenetetracarboxylic dianhydride and 3,4,7,8-naphtalenetetracarboxylic dianhydride. A notable figure of merit is that lattice matching is not necessarily required [6] to join two types of organic materials or to grow an organic heterostructure on an inorganic substrate. This has opened a new promising possibility to produce strongly ordered heterostructures with a wide choice for their composition most suitable to oriented practical purposes.

Optical properties of inorganic semiconducting materials near the band gap are mainly due to Wannier–Mott excitons which have large Bohr radii and therefore are very sensitive to external perturbations. Having large radii also means a deviation from the boson character at low concentration because of the kinematical interexciton interaction (see, e.g., Ref. [7] and references therein) bringing about an additional source of nonlinearity. In organic materials, on the other hand, the physics is known to be essentially different compared to that in inorganic semiconductors since in this case the primarily important elementary excitations are Frenkel excitons which possess small radii and spatial dispersion but, instead, considerable oscillator strengths. One

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[1] Permanent address: National Center for Natural Sciences and Technology, Institute of Physics, P.O. Box 429 Bo Ho, Hanoi 10000, Vietnam.

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could think of generating quasiparticles with radii as large as those of Wannier–Mott excitons and oscillator strengths as considerable as those of Frenkel excitons. Such hypothetical hybrid excitons have in fact been theoretically investigated for the first time in a pair of organic–inorganic quantum wells [8] and quantum wires [9]. Although composite structures like those proposed in Refs. [8,9] have not yet been prepared, further theoretical studies are worth doing because of the unique characteristics of such structures. Following the idea mentioned in Ref. [9] we wish to extend the model to a planar array of alternating organic and inorganic quantum wires. Since experiments should rather be carried out on wire arrays than on an isolated pair of wires to enhance the effect caused by the interwire interaction, the pair-to-array extension has its own virtue and is very meaningful from both an academic and a practical point of view. We derive analytical expressions for the interaction between wires of the same or different types. The eigenproblem of the whole composite structure seems complicated but is solved exactly with the global interwire interactions taken rigorously into account. Qualitatively different dispersions of the eigenmodes are obtained for different exciton dipole moment configurations.

Let us consider a planar composite array of parallel quantum wires as depicted in Fig. 1. An inorganic quantum wire (IQW) is represented by a solid line labelled an odd number $2n-1$ with $n=1, 2, \dots, N$ and $2N$ specifying the size of the structure. A dashed line with a label $2n$ represents an organic quantum wire (OQW). Denote by d the interwire spacing. The intrawire interaction gives rise to the one-dimensional (1D) exciton of the Wannier–Mott type in the IQW and of the Frenkel type in the OQW. If the energies ϵ_{w} of the Wannier–Mott exciton and ϵ_{f} of the Frenkel exciton are much larger than the interaction energies g_{ff} between two OQWs, g_{ww} between two IQWs and g_{fw} between an OQW and an IQW the Hamiltonian of the whole composite structure can be written in the 1D-exciton-based representation as

$$\begin{aligned} H = \sum_k \sum_n \Big(& \epsilon_{\mathrm{w}}(k) w^+_{2n-1k} w_{2n-1k} + \epsilon_{\mathrm{f}}(k) f^+_{2nk} f_{2nk} + g_{\mathrm{fw}}(d,k)(f^+_{2nk} w_{2n-1k} + \mathrm{h.c.}) \\ & + \sum_{n'}{}' \{ g_{\mathrm{ww}}(2\,|n-n'|\,d,k) w^+_{2n'-1k} w_{2n-1k} + g_{\mathrm{ff}}(2\,|n-n'|\,d,k) f^+_{2n'k} f_{2nk} \\ & + \tfrac{1}{2} [g_{\mathrm{wf}}(|2(n-n')-1|\,d,k) f^+_{2n'k} w_{2n-1k} + g_{\mathrm{wf}}(|2(n-n')+1|\,d,k) f^+_{2nk} w_{2n'-1k} + \mathrm{h.c.}] \} \Big), \end{aligned} \tag{1}$$

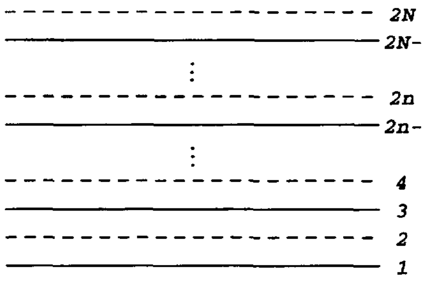
where we are only interested in the lowest energy Wannier–Mott and Frenkel exciton and denote by w_{2n-1k}, w^+_{2n-1k} and f_{2nk}, f^+_{2nk} their operators at IQW $2n-1$ and OQW $2n$, respectively. $\boldsymbol{k}$ is the 1D wave vector of the exciton motion along the wire direction. $\Sigma'_{n'}$ means exclusion of the term with $n'=n$ while summing over n'. The interwire interaction depends not only on $\boldsymbol{k}$ and separation between wires but also on the orientations of the electric dipole moment of the exciton. Suppose that the dipole moments for the Wannier–Mott exciton $\boldsymbol{d}_{\mathrm{w}}$ and the Frenkel one $\boldsymbol{d}_{\mathrm{f}}$ in all wires are oriented parallel to each other. We distinguish three orientation configurations in which the dipole moments point to the x axis (X), y axis (Y) and z axis (Z). Choosing the z axis to coincide with the wire direction, the y axis perpendicular to the wires but lying in the array plane and the x axis perpendicular to that plane, the interwire interaction can be factorized in the form

$$g^{(P)}_{\zeta\xi}(l,k) = \gamma_{\zeta\xi}(l) F^{(P)}(kl), \tag{2}$$

with ζ, $\xi = \mathrm{w}$ or f, $P = X$, Y or Z and l the interwire distance. Our detailed calculations yield (for related references see, e.g., Refs. [9,10])

$$\gamma_{\mathrm{fw}}(l) = \frac{4\,|\Phi_\nu(0)|\,d_{\mathrm{f}} d_{\mathrm{w}}}{(\varepsilon_{\mathrm{f}} + \varepsilon_{\mathrm{w}})\sqrt{a}\,l^2}, \tag{3}$$

$$\gamma_{\mathrm{ww'}}(l) = \frac{2\,|\Phi_\nu(0)|^2 d_{\mathrm{w}} d_{\mathrm{w'}}}{\varepsilon_{\mathrm{w}} l^2}, \tag{4}$$



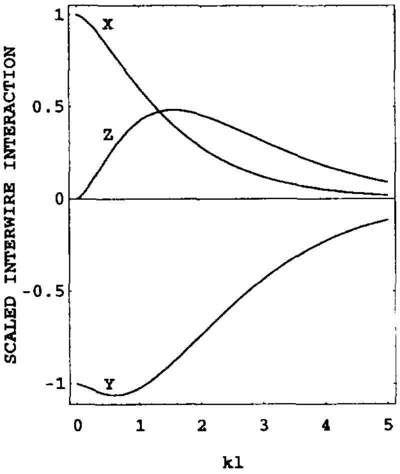


Fig. 1. Planar array of alternating organic (dashed lines) and inorganic (solid lines) quantum wires.

Fig. 2. Scaled interwire interaction $F^{(P)}(kl)/E_{3D}$ as functions of kl for the X-, Y- and Z-configuration of the dipole moment orientation.

$$\gamma_{ff'}(l) = \frac{2d_f d_{f'}}{\varepsilon_f a l^2}, \tag{5}$$

$$F^{(X)}(kl) = klK_1(lk), \tag{6}$$

$$F^{(Y)}(kl) = -F^{(X)}(kl) - F^{(Z)}(kl), \tag{7}$$

$$F^{(Z)}(kl) = k^2 l^2 K_0(kl). \tag{8}$$

In the above formulae $\Phi_\nu(0)$ is the real space envelope function at the origin describing the electron–hole relative motion within a Wannier–Mott exciton in quantum state ν. According to Refs. [11–13], $\Phi_\nu(0) = W_{\nu,1/2}(R_\nu)/[\nu r_{3D}\int_{R_\nu}^{\infty}|W_{\nu,1/2}(\sigma)|^2\,d\sigma]^{1/2}$ with $R_\nu = 0.6R/\nu r_{3D}$, $W_{\nu,1/2}$ the Whittaker function, r_{3D} the 3D exciton Bohr radius, R the IQW radius and for the lowest exciton state ν satisfies the relation $2\nu\,\ln(R_\nu) = -1$. ε_w (ε_f) is the dielectric constant of the IQW (OQW) material and a the 1D lattice constant of the OQW. The dimensionless factors $F^{(P)}$ characterize the dipole moment orientation configuration and are analytically expressed in terms of the modified Bessel functions of the second kind K_0 and K_1. Fig. 2 shows that for a large wave vector $\boldsymbol{k}$ or/and a large separation l the interwire interactions of all types tend to vanish whereas their behavior is strongly distinct for different orientation configurations near the Brillouin zone center where optical phenomena occur. The Z-configuration interwire interaction vanishes at $k = 0$ resembling the situation of multiple quantum wells [14–18]. The X- and Y-configuration interwire interactions are nonzero and have opposite signs near $k = 0$. As a rule [19], $F^{(X)} + F^{(Y)} + F^{(Z)} = 0$ everywhere. Such behavior of the interwire interactions should essentially influence the dispersion relations and, consequently, also the optical responses of the composite structure under consideration. The strength of the interwire interaction is dictated by the material parameters and measured by the factors $\gamma_{\zeta\xi}$ which are independent of the dipole moment orientation configuration. For an estimate we take for GaAs/Ga$_x$Al$_{1-x}$As IQWs $m_e/m_0 = 0.065$, $m_h/m_0 = 0.5$ (m_e (m_h) and m_0 are the electron (hole) effective mass and the mass of a free electron), the band gap energy $E_g = 1.5$ eV, $\varepsilon_w = 10$, $R = 0.1r_{3D}$, $d_w = 10$ D and assume an infinite quantum confinement potential. For the OQW we take

$\varepsilon_f = 3$, $a = 8$ Å and $d_f = 12$ D. Then for $l = 5R$ we get $\gamma_{fw}(l) = 0.56$ meV, $\gamma_{ff}(l) = 3.58$ meV and $\gamma_{ww}(l) = 0.12$ meV. We see that at the same separation the strongest interaction is between two OQWs and the weakest one is between two IQWs. The numerical evaluation also indicates that $\gamma_{ff}(2l) \approx \gamma_{ww}(l)$, etc. These reveal that the nearest wire approximation usually applicable in conventional structures consisting only of one type of wires is not an accurate one in the composite structure like that considered here. In the latter structure care must be taken in deciding how many nearest wires are "good" for the properly approximate numerical calculation. A delicate thing is that the "good" number of nearest wires differs for the IQWs and the OQWs and, moreover, varies from material to material. In our treatment below we shall account for the interaction between all wires, i.e., the interwire interaction is taken into account globally thus avoiding the problem of the "good" number of nearest wires mentioned above.

Returning to the Hamiltonian, I note that, when the periodicity of the whole composite structure with a period $2d$ is used, H can exactly be diagonalized,

$$H = \sum_{\mu q k} \Omega_\mu(q, k) \mathscr{B}^+_{\mu q k} \mathscr{B}_{\mu q k}, \qquad \mu = 1, 2 \tag{9}$$

by the following transformation,

$$\mathscr{B}_{\mu q k} = \frac{1}{\sqrt{N}} \sum_n e^{-2indq} \left[\mathscr{U}_\mu(q, k) w_{2n-1k} + \mathscr{V}_\mu(q, k) f_{2nk} \right], \tag{10}$$

where

$$\mathscr{U}_\mu(q, k) = \sum_{\alpha = 1,2} U_{\mu\alpha}(q, k) u_\alpha(k), \tag{11}$$

$$\mathscr{V}_\mu(q, k) = \sum_{\alpha = 1,2} U_{\mu\alpha}(q, k) v_\alpha(k), \tag{12}$$

$$u_\alpha(k) = \left(1 + \frac{[g_{fw}(d, k)]^2}{[E_\alpha(k) - \epsilon_f(k)]^2} \right)^{-1/2}, \tag{13}$$

$$v_\alpha(k) = \frac{u_\alpha(k) g_{fw}(d, k)}{E_\alpha(k) - \epsilon_f(k)}, \tag{14}$$

with

$$E_\alpha(k) = \tfrac{1}{2} \left\{ \epsilon_f(k) + \epsilon_w(k) + (-1)^\alpha \sqrt{[\epsilon_f(k) - \epsilon_w(k)]^2 + 4[g_{fw}(d, k)]^2} \right\}, \tag{15}$$

and

$$U_{\mu 1}(q, k) = \left(1 + \frac{|\mathscr{E}_{12}(q, k)|^2}{[\Omega_\mu(q, k) - \mathscr{E}_1(q, k)]^2} \right)^{-1/2}, \tag{16}$$

$$U_{\mu 2}(q, k) = \frac{U_{\mu 1}(q, k) \mathscr{E}_{12}(q, k)}{\Omega_\mu(q, k) - \mathscr{E}_1(q, k)}, \tag{17}$$

with

$$\mathscr{E}_\alpha(q,k)=E_\alpha(k)+4\sum_{\rho=1}^{N-1}G_{\alpha\alpha}(\rho,d,k)\cos(2\rho dq), \tag{18}$$

$$\mathscr{E}_{\alpha\alpha'}(q,k)=\sum_{\rho}{}'G_{\alpha\alpha'}(\rho,d,k)\mathrm{e}^{2\mathrm{i}\rho dq}, \tag{19}$$

where Σ'_ρ means summing over $\rho=\pm1, \pm2,\dots,\pm(N-1)$ and

$$\begin{aligned}G_{\alpha\alpha'}(\rho,d,k)=\tfrac{1}{2}\big[&g_{\mathrm{ww}}(2|\rho|d,k)u_\alpha(k)u_{\alpha'}(k)+g_{\mathrm{ff}}(2|\rho|d,k)v_\alpha(k)v_{\alpha'}(k)\\&+g_{\mathrm{wf}}(|2\rho-1|d,k)u_\alpha(k)v_{\alpha'}(k)+g_{\mathrm{wf}}(|2\rho+1|d,k)v_\alpha(k)u_{\alpha'}(k)\big],\end{aligned} \tag{20}$$

$$\Omega_\mu(q,k)=\tfrac{1}{2}\Big[\mathscr{E}_1(q,k)+\mathscr{E}_2(q,k)+(-1)^\mu\sqrt{[\mathscr{E}_1(q,k)-\mathscr{E}_2(q,k)]^2+4|\mathscr{E}_{12}(q,k)|^2}\Big]. \tag{21}$$

In the above expressions a new 1D wave vector $\boldsymbol{q}$ appears that is perpendicular to the wire direction and describes hopping from wire to wire caused by the presence of the interwire interaction. The allowed values of q can be found for large N from the cyclic boundary condition yielding $q\equiv q_m=m\pi/Nd$ with $m=0, 1, 2,\dots,N-1$. Hence, for a given value of k, there are $2N$ eigenmodes in the whole composite structure whose dispersion relations are determined by Eq. (21). It is easy to verify that our formal result for $N=1$ recovers the hybrid excitons predicted in Ref. [9]. In an isolated IQW–OQW pair the two hybrid excitons reside within the pair and are independent. When N such pairs are packed together a hybrid exciton is mixed with the other hybrid exciton in the same pair as well as with those in all other pairs to form the eigenmodes $\Omega_\mu(q, k)$ of the whole structure which are hopping throughout all wires and possess features of both Wannier–Mott and Frenkel excitons in a different way than the hybrid excitons. For $N=10$, $d=5R$, $\epsilon_{\mathrm{f}}^{(P)}-\epsilon_{\mathrm{w}}(0)=1$ meV (the electron–hole exchange interaction in the IQW and the dispersion of the Frenkel exciton are neglected for simplicity) and for the material parameters mentioned above the dispersions of two eigenmodes $\{\mu=1, q_0\}$ and

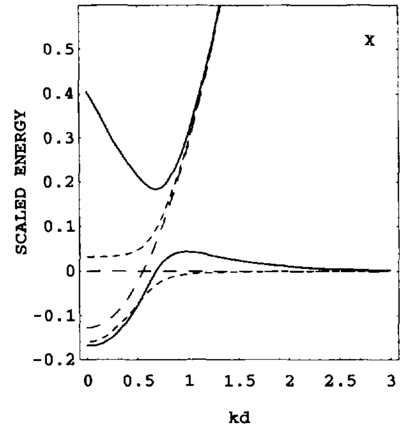


Fig. 3. X-configuration dispersion relations of the Frenkel exciton (long-dashed horizontal line), the Wannier–Mott exciton (long-dashed curve), hybrid excitons (short-dashed curves) and eigenmodes (solid curves) of the composite structure with $q=q_0$. All energies are scaled to $E_{3\mathrm{D}}$ and counted from the Frenkel exciton energy which is taken as the origin of the energy axis. For the numerical parameters used for plotting see text. At large kd all the modes coincide with the bare excitons while for small kd the modes differ strongly due to the global interwire interaction.

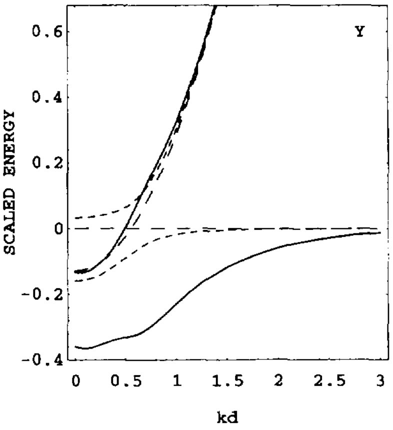
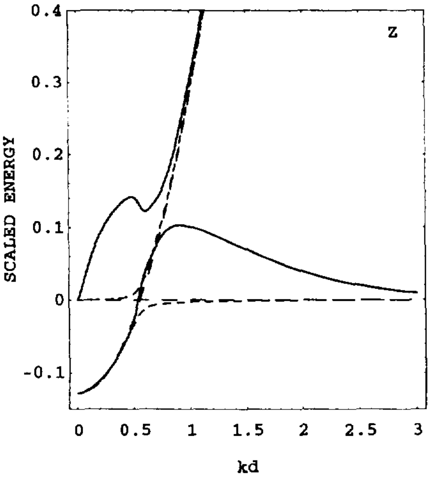


Fig. 4. Same as in Fig. 3 but for the Y-configuration.



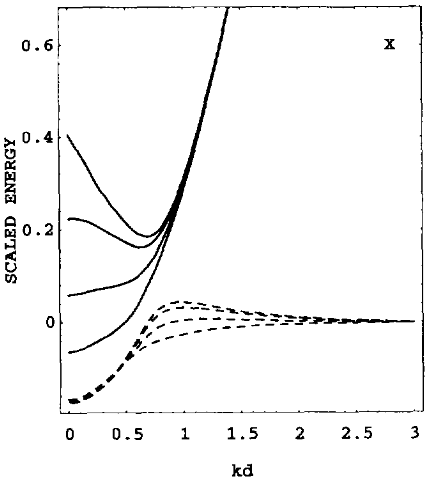
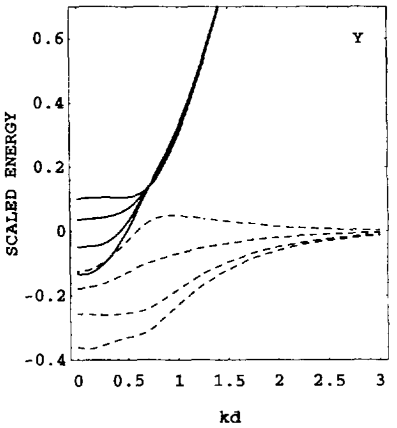


Fig. 5. Same as in Fig. 3 but for the Z-configuration.

Fig. 6. X-configuration scaled eigenmode energies $(\Omega_\mu(q, k) - \epsilon_f^{(X)})/E_{3D}$ as functions of kd for $\mu = 1$ (dashed curves), $\mu = 2$ (solid curves) and $q = q_0$, q_1, q_2 and q_3 (downwards).

$\{\mu = 2, q_0\}$ are plotted in Figs. 3, 4 and 5 for the X-, Y- and Z-configurations, respectively. Also illustrated for comparison are the dispersions of the bare excitons (long-dashed curves) and the hybrid ones (short-dashed curves). The distinctions between the excitons and the eigenmodes as well as between different configurations are clearly visual. To see the q-dependence we draw in Figs. 6, 7 and 8 the dispersions of 8 eigenmodes $\{\mu = 1, q_0\}$, $\{\mu = 1, q_1\}$, $\{\mu = 1, q_2\}$, $\{\mu = 1, q_3\}$ (dashed curves) and $\{\mu = 2, q_0\}$, $\{\mu = 2, q_1\}$, $\{\mu = 2, q_2\}$, $\{\mu = 2, q_3\}$ (solid curves) for the X-, Y- and Z- configurations, respectively. The specific k-dependence of the global interwire interaction governs the dispersion relation for each dipole moment orientation configuration in



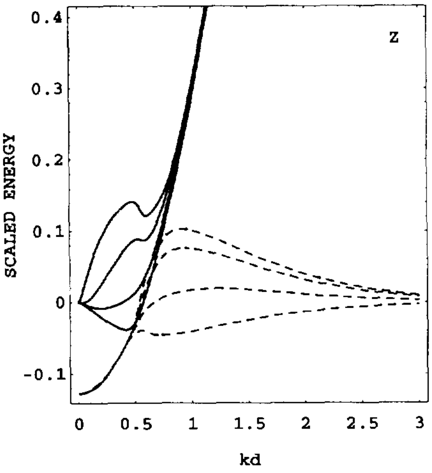


Fig. 7. Same as in Fig. 6 but for the Y-configuration and the word "downwards" is replaced by "upwards".

Fig. 8. Same as in Fig. 6 but for the Z-configuration.

its own manner as seen from the figures. Due to globally accounting for the interwire interaction the resulting eigenmode dispersion may exhibit maxima or/and minima away from the point $k = 0$. These unusual shapes of the dispersion are expected to greatly modify the optical responses of the composite structure as compared to the conventional array of inorganic semiconducting quantum wires [20–22]. It would be premature to say what the benefits of the modification are before an accurate calculation of the optical responses has been performed using the results obtained in this Letter for the electronic states.

For the material parameters used here the 1D exciton energy is of about 6 eV whereas the largest interwire interaction energy is of about 3.5 meV. This justifies the 1D-exciton-based representation (Eq. (1)). In most practical cases this remains a good representation. The eigenmodes and their associated optical responses are experimentally observable if the 1D exciton damping is small compared with the interwire interaction energy. As learnt from Eqs. (3)–(5) the smaller the IQW radius, the dielectric constants, the OQW lattice constant, the wire–wire separation and/or the larger the dipole moments the stronger the interwire interaction strength. Usually the exciton damping is of the order of 1 meV so that the system parameters should be carefully chosen to have the interwire interaction energy to be greater than that amount. (Note, the parameters used in Ref. [9] should give $\Gamma \approx 0.54$ meV instead of 5.4 meV as was ten times overestimated there.) Polaritons, polariton solitons and superradiance in the composite array of wires would be very interesting topics because the spatial dispersion effect [23–25] would not be weak. A similar scheme of treatment may be applied to arrays of alternating organic and inorganic quantum wells and quantum dots which would bring about non-similar physical pictures because the interwell and interdot interactions are qualitatively different from the interwire one. Though random assemblies of quantum dots were prepared a long time ago, periodic arrays of quantum dots have just recently been fabricated [26] and theoretically investigated [27,28]. Production of organic–inorganic composite heterostructures is still not possible. Nevertheless, their unique physical properties deserve any advance theoretical study.

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