Electronic correlation in the shake-up process in atomic doubly excited asymmetric states

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The effects of the electronic correlation in the shake-up process of atomic doubly excited asymmetric states have been investigated by using a nondegenerate perturbative method. It is shown that the overlap spectrum and the recently observed abnormal spectrum can be described by the same theoretical framework. The quantitative intrinsic relation between the well known overlap formula and the electronic correlation has been revealed analytically. The scope for applying the overlap formula has been discussed. The shake-off process has also been discussed as a continuum case of the shake-up process. It is shown that the escape electron in a shake-off process of a higher-l state or with a higher escape energy tends to increase its angular momentum.

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I. INTRODUCTION

The dielectronic correlation plays the central role in understanding the electronic correlations in a complex atom. While the two electron atoms serve as the prototype for the investigation of the dielectronic correlation, other complex atoms with more than two electrons exhibit generally less influence by the dielectronic correlations, because the extra electron(s) tends to reduce the importance of the dielectronic correlation. On the other hand, the effect also makes it possible to treat the correlation in a perturbative way by means of the multipole expansion of the dielectronic correlation. This method will be used in this paper to study the dielectronic correlation in doubly excited asymmetric states of alkali-earth atoms.

For alkali-earth atoms, most of the experimental investigations of the electronic correlation were performed on the asymmetric states $NLnl(N<n)$ by means of the isolated-core excitation (ICE) technique through laser excitation [1–8]. In the ICE description of the excitation process, only the inner electron is acted on by the photon dipole operator, while the outer electron may be shaken from the initial Rydberg orbit into another Rydberg orbit or remains unchanged. The spectrum related to this scheme is called the ICE spectrum. The process excluding the trivial case where the outer electron orbit remains unchanged is usually called the ''shake-up'' process. A typical type of spectrum for the shake-up process is the so-called ''overlap'' spectrum. Based on a phenomenological description for the overlap spectrum, the outer electron is simply ''projected'' from an initial Rydberg orbit to a final Rydberg orbit. This description is indeed a brief summary phenomenologically according the framework of MQDT. Although MQDT can reproduce most of the observed spectra, it does not give us any hint in physics by which to understand how the outer electron is forced into a different orbit in the excitation process. From the integral for the ''projection,'' it can be found that the outer part of the outer electron wave function in the configuration space [9] dominates the line strength in the overlap spectrum. It looks as if there is no effect from electronic correlation in the excitation process. This fact seems in contradiction to the wave packet experiment [10] where the shake-up process can take place only when the outer electron is closed to the inner electron.

Recently, abnormal types of spectra were observed in the shake-up process of high-l doubly excited asymmetric states in strontium [8], which show different structures from the overlap spectrum and reveal the importance of the electronic correlation in the excitation process. In this paper we propose to study the electronic correlation effect in the shake-up process in a perturbative way, and to figure out the quantitative intrinsic relation between the electronic correlation and the overlap integral for the overlap spectrum. It will be shown that the abnormal types of spectra and the overlap spectrum can be expressed in a unified way within the same theoretical framework. In Sec. II, we will describe the theoretical description for the shake-up process. In Sec. III, we will discuss the scope for applying the overlap formula and the shake-off process.

II. THEORY

For simplicity, we ignore the electronic correlation effects in the initial state for the ICE process and assume that the electronic correlation in the final state is weak. The spin-orbit coupling will not be included in our discussion, while it should be considered in application and is easily done. The line broadening effects due to the interaction between discrete and continuum energy levels will not be accounted for in our discussion. We will use a nondegenerate perturbative configuration interaction (CI) method to study the electronic correlation. This method is particularly feasible for high-l asymmetric states (planetary states). However, the physical mechanism discussed here is also expected to hold for other doubly excited asymmetric states with strong electronic correlation. Only one photon excitation process will be considered here. Multiphoton excitation processes can be derived based on the one-photon case.

In our discussion, we will use the wave functions (NL) of alkali-earth ions (alkalilike) as the wave functions of the inner electron and the hydrogen wave functions $(nl,\ n\gg N,\ l>1)$ as the wave functions of the outer electron to describe the asymmetric atomic state for the unperturbed (correlation-free) case. The only influence of the $2+$ core taken into

account is that it removes the l degeneracy of the inner electron, so that the ionic energy levels NL in our discussion are nondegenerated, which thus allows the application of nondegenerate perturbation theory. Atomic units will be used unless otherwise specified.

A. Electronic correlation in the shake-up process

For an ICE spectrum from an initial state $N_0L_0n_0l_0$ to a final state $NLnl$, in the absence of the electronic correlation, we have

$$\begin{aligned} n&=n_0,\\ l&=l_0,\\ L&=L_0\pm 1 \end{aligned} \tag{1}$$

for the observable resonance. The observed lines are identical to the ionic lines $N_0L_0\rightarrow NL$. We assume only one line will be observed in this case in order to simplify our discussion. The case of multiple lines (different N,L) can be obtained by summing the contributions from each line. Due to the electronic correlation, Eq. (1) is not always valid for all resonances. We label the final state satisfying Eq. (1) $N_1L_1n_0l_0$. The intensity of this resonance will not be discussed here. From the perturbation theory, other observed resonances for $NLnl$ should be due to the perturbation between $NLnl$ and $N_1L_1n_0l_0$. The perturbation arises from the electronic correlation which can be expressed by means of the spherical harmonics, i.e.,

$$\frac{1}{r_{12}}=\sum_{k=0}\frac{r_<^k}{r_>^{k+1}}P_k(\cos\theta_{12}). \tag{2}$$

Explicitly, the electronic wave function for a final state $NLnl$ can be written as

$$\Psi=|NLnl\rangle+c_n|N_1L_1n_0l_0\rangle+\cdots, \tag{3}$$

$$c_n=\frac{1}{E^n_{n_0}}\langle N_1L_1n_0l_0|S|NLnl\rangle. \tag{4}$$

Here S is the perturbation between the two configurations, which may include the direct perturbation and the cross-term perturbation mediated by other configurations. $E^n_{n_0}$ is the energy difference between the perturbing states. The observed line strength for $NLnl$ is

$$P\sim|c_n\langle N_0L_0|r|N_1L_1\rangle|^2. \tag{5}$$

B. Line strength for the overlap spectrum

1. $NL=N_1L_1$, $l=l_0$

Before deriving the line strength for the overlap spectrum from Eq. (5), let us recall the widely used overlap formula

$$P_o\sim|\langle N_0L_0|r|N_1L_1\rangle\langle n_0l_0|\nu l_0\rangle|^2, \tag{6}$$

for the transition probability in the shake-up process from an initial state $N_0L_0n_0l_0$ to a final states $N_1L_1nl_0(N_0;N_1\ll n_0;n)$. The wave function of the outer electron $|\nu l_0\rangle$ is a QDT type channel wave function. Equation (6) is a good approximation when the outer electron experiences vanishing electronic correlation in most of its time. This condition implies $l_0\ll n_0;n$, for which a good approximation for the overlap integral in Eq. (6) is [7]

$$\langle n_0l_0|\nu l_0\rangle=\frac{2\sqrt{\nu n_0}\sin\pi(\nu-n_0)}{\pi(\nu^2-n_0^2)}, \tag{7}$$

where $\nu=n^*$. It can be found that the overlap formula reflects the electronic correlation only through the energy shift of the level, while Eq. (4) shows that the observed resonance is a result of the perturbation from the individual configuration. We will show quantitatively in the following the intrinsic relation between them.

From Eq. (2) we know that the main contribution for Eq. (4) arises from the inner part of the outer wave function (i.e., from small $r_>$). For the final state $N_1L_1nl_0$ with $l_0\ll n_0;n$, Equation (4) can be approximated to

$$c_n\simeq\frac{2(n/n_0)^{3/2}}{1/n_0^2-1/n^2}\langle N_1L_1nl_0|S|N_1L_1nl_0\rangle. \tag{8}$$

The approximation is based on the fact that the inner part of the energy-normalized wave function is almost the same for the outer electron in two orbits nl_0 and n_0l_0. On the other hand, the perturbative energy shift of $N_1L_1nl_0$ due to the electronic correlation is

$$\Delta E_n^{(1)}=\langle N_1L_1nl_0|S|N_1L_1nl_0\rangle\simeq\frac{\nu-n}{n^3}. \tag{9}$$

From Eqs. (8) and (9), we have

$$c_n\simeq\frac{2\sqrt{nn_0}(\nu-n)}{n^2-n_0^2}. \tag{10}$$

Substituting Eq. (10) into Eq. (5), we obtain approximately the same result as the overlap formula from Eqs. (6) and (7), since $|\sin\pi(\nu-n_0)|\simeq|\pi(\nu-n)|$ and $(\nu^2-n_0^2)\simeq(n^2-n_0^2)$, owing to the weak perturbation ($|\Delta E_n^{(1)}|\ll 1/\nu^3$).

2. $NL\neq N_1L_1$ or/and $l\neq l_0$

For these cases the overlap formula adopts an MQDT form

$$P_o^{\mathrm{MQDT}}\sim\rho_nP_o, \tag{11}$$

where ρ_n is the percentage of $|N_1L_1\nu l_0\rangle$ mixed into $|NLnl\rangle$, $\rho_n\ll 1$. In perturbation theory, ρ_n can be expressed as

$$\rho_n=\sum_i\left|\frac{1}{E_i^n}\langle N_1L_1il_0|S|NLnl\rangle\right|^2. \tag{12}$$

The summation can be also extended to include the contribution from the continuum state. Here we discuss only the

case where $|NLnl\rangle$ is located between two Rydberg states $|N_1L_1ml_0\rangle$ and $|N_1L_1(m+1)l_0\rangle$ so that we can apply the perturbation theory for discrete states, i.e., $m<\nu<(m+1)$, where ν denotes the effective principle quantum number of an independent electron scaled in the $|N_1L_1\nu l_0\rangle$ channel for the $|NLnl\rangle$ state. For $l_0 \ll n_0;m$, we can apply an approximation similar to that made in Eq. (8). We have

$$\rho_n \simeq \sum_i \left| \frac{(n_0/i)^{3/2}}{E_i^n} \langle N_1L_1n_0l_0|S|NLnl\rangle \right|^2. \tag{13}$$

Substituting Eqs. (6), (7), and (13) into Eq. (11), we have

$$P_o^{\mathrm{MQDT}} \sim |c_n\langle N_0L_0|r|N_1L_1\rangle|^2 \sum_i \left[\frac{2\sqrt{\nu i}\sin\pi(\nu-n_0)}{\pi(\nu^2-i^2)} \right]^2, \tag{14}$$

where c_n is given by Eq. (4). This result is approximately the same as Eq. (5) since the summation in Eq. (14) is closed to 1.

It should be noted that Eq. (13) is not valid for some special final states (e.g., $L=L_1\pm1$, $l=l_0\pm1$) with $n\sim n_0$ or $n=m;m+1$, because $\langle N_1L_1il_0|S|NLnl\rangle$ has a minimum for those states around $i=n$ due to the orthogonal properties of the matrix elements in hydrogen wave functions [8,11]. For that case the overlap formula is not valid.

C. Line strength for the abnormal spectrum

It has been known that the inner part of the outer electron wave function dominates the electronic correlation with the inner electron and this correlation can be reflected through the phase shift in the outer part, which is referred to here as ''propagation.'' For an overlap spectrum it can be said that the propagation is ''undistorted'' so that the overlap formula, which considers the outer part only, can reproduce the spectrum well. The prerequisite for applying the overlap formula, as discussed above, is the approximation made in Eq. (8) or (13), and in the MQDT case with some additional requirements for n. Furthermore, for applying the MQDT type of overlap formula, the two channels $|N_1L_1il_0\rangle$ and $|NLnl\rangle$ should be degenerated in the energy region concerned. In other cases, the propagation of the electronic correlation to the outer part is said to be ''distorted.'' The respective spectrum is called here an ''abnormal'' spectrum compared to the overlap spectrum. In some cases, a modified overlap integral based on a dynamic potential can well reproduce the abnormal spectrum [3]. Generally for an abnormal spectrum, there is no phenomenological formula such as the overlap formula. The line strength should be calculated from Eq. (5) as already done in Ref. [8].

III. DISCUSSION

A. Overlap spectrum or abnormal spectrum?

The criterion for distinguishing the overlap and the abnormal spectrum has been given in the above discussion. From the approximations made in Eqs. (8) and (13), it can be seen that low-l states are more feasible for applying the overlap formula. Here we present numerical examples to show the evolution from the overlap to the abnormal spectrum for the excitation of a single channel $|N_1L_1nl_0\rangle$. The penetration between the inner and outer wave functions will complicate our calculation. We assume there is no penetration between two electrons. As a result, the monopole perturbation in Eq. (2) is excluded. Thus there are two main types of perturbations which can cause the shake-up excitation of $|N_1L_1nl_0\rangle$, i.e., the quadrupole perturbation (for $L_1\neq0$) and the cross-term dipole perturbation [8].

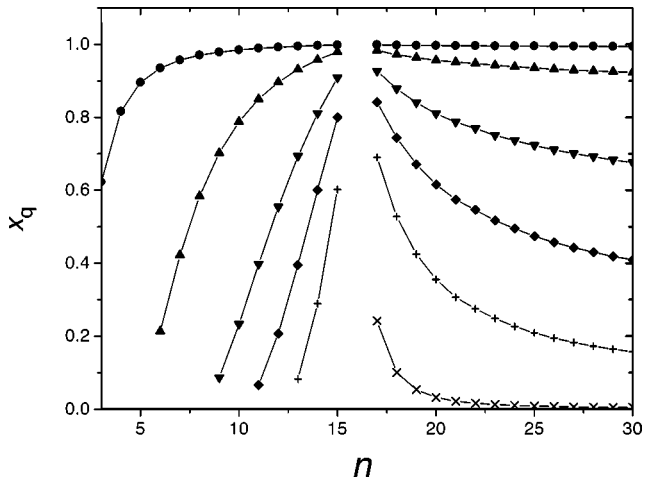

FIG. 1. Comparison of the oscillator strength from the perturbative calculation with that from the overlap formula in the case of quadrupole perturbation for $NL=N_1L_1$, $n_0=16$ and different n, l_0. $l_0=2,5,8,10,12,15$ for the curves from the top to the bottom sequentially. A value of x_q closed to 1 indicates a good approximation of the overlap formula.

1. Quadrupole perturbation

From Eqs. (4) and (8), we have

$$x_q = \frac{P^q}{P_o^q} \simeq \left| (n_0/n)^{3/2} \frac{\langle n_0l_0|1/r^3|nl_0\rangle}{\langle nl_0|1/r^3|nl_0\rangle} \right|^2. \tag{15}$$

P^q is given by Eq. (5) and P_o^q is given by the overlap formula. When the overlap formula holds, $x_q\approx1$. Otherwise the abnormal spectrum will be observed. Figure 1 gives the values of x_q as a function of n for various l_0 with $n_0=16$.

2. Cross-term dipole perturbation

Similar to Eq. (15), we have

$$x_{dd} = \frac{P^{dd}}{P_o^{dd}} \simeq \left| (n_0/n)^{3/2} \frac{T_{n_0n}}{T_{nn}} \right|^2, \tag{16}$$

where

$$T_{in} = \sum_{n',l'} \frac{\langle il_0|1/r^2|n'l'\rangle\langle n'l'|1/r^2|nl_0\rangle}{E_{n'n}}; \quad i=n_0,n. \tag{17}$$

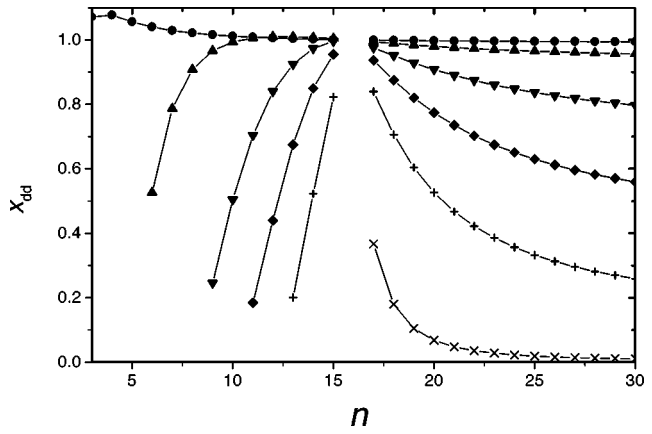

FIG. 2. Similar to Fig. 1, but for the case of cross-term dipole perturbation. A value of x_{dd} closed to 1 indicates a good approximation of the overlap formula.

Here $E_{n'n}$ is the energy difference between $|N_1L_1nl_0\rangle$ and $|N'L'n'l'\rangle$. We assume the main dipole perturbation is from $|N'L'n'l'\rangle$ for $|N_1L_1nl_0\rangle$ ($l'=l\pm1$). The summation of n' includes the contribution from the continuum states. To further simplify our discussion, we assume the main contribution in Eq. (17) arises from those states with $E_{n'n} \approx E_{N_1L_1,N'L'}$ (the energy difference between the ionic states $|N_1L_1\rangle$ and $|N'L'\rangle$). Then Eq. (17) can be reduced to

$$T_{in} \simeq \frac{2}{E_{N_1L_1,N'L'}} \langle il_0|1/r^4|nl_0\rangle; \quad i=n_0,n. \tag{18}$$

Substituting Eq. (18) into Eq. (16), we obtain

$$x_{dd} \simeq \left| (n_0/n)^{3/2} \frac{\langle n_0l_0|1/r^4|nl_0\rangle}{\langle nl_0|1/r^4|nl_0\rangle} \right|^2. \tag{19}$$

Similarly, the application of the overlap formula requires $x_{dd} \approx 1$. Figure 2 gives the values of x_{dd} as a function of n for various l_0 with $n_0=16$.

3. Discussions

Figures 1 and 2 show that the scope for applying the overlap formula strongly depends on l_0. The latter case is more feasible for the overlap formula. In both cases, $n>n_0$ seems to be more feasible than $n<n_0$ with the same $|n-n_0|$ for the overlap formula. At high-l states, both cases show significant abnormal behaviors. Note that the trivial case $n=n_0$ is not included in our discussion. A real spectrum is composed from the constructive or destructive interference of the two perturbations. From Eqs. (15), (16), (18), and (19) the relative amplitude of the two perturbations can be approximated as

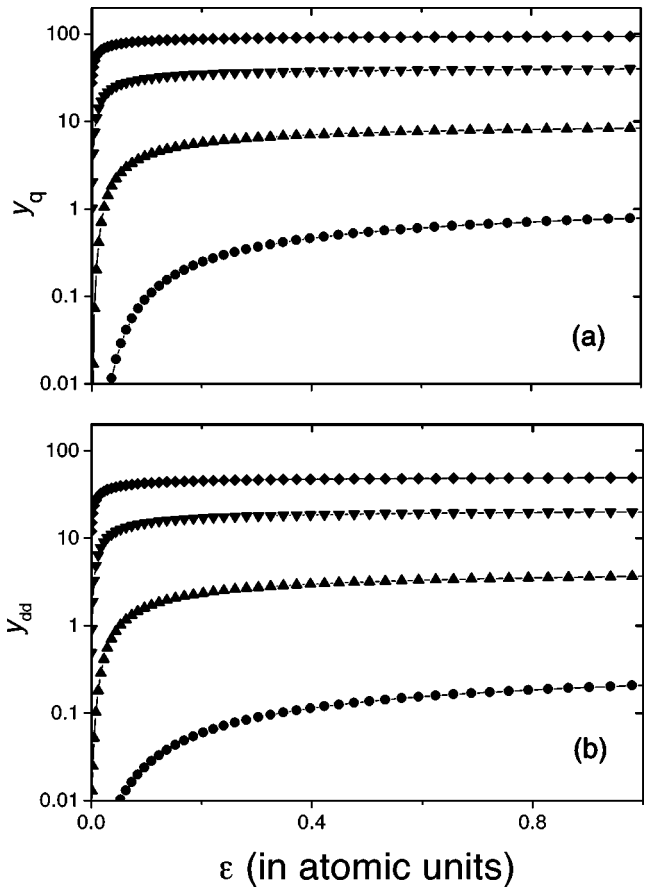

FIG. 3. The ratio of the probabilities of the escape electron with an angular momentum l_0+2 and l_0 in the shake-off process of the initial state with $n_0=16$ due to (a) quadrupole perturbation, (b) cross-term dipole perturbation, according to Eqs. (21) and (22). $l_0=2,5,10,15$ for the curves from the bottom to the top sequentially in each of the figures. Note that the ratios of the angular coefficients B_q and B_{dd} in Eqs. (21) and (22) are approximated to 1.

$$R = \sqrt{\frac{P^q}{P^{dd}}} \approx \left| A_{q,dd} \frac{E_{N_1L_1,N'L'}\langle nl_0|1/r^3|nl_0\rangle}{2\langle nl_0|1/r^4|nl_0\rangle} \right| \sqrt{\frac{x_q}{x_{dd}}},$$

$$= \left| A_{q,dd} \frac{E_{N_1L_1,N'L'}(l_0+3/2)(l_0-1/2)}{[3-l_0(l_0+1)/n^2]} \right| \sqrt{\frac{x_q}{x_{dd}}}, \tag{20}$$

where $A_{q,dd}$ is decided by the radial integrals of the inner electron and the angular momentum coupling coefficients, and usually has the order of 1. It shows lower-l cases have more cross-term perturbation characters than higher-l cases in the spectrum and vise versa. For higher excited orbital energy of the inner electron, it is expected that the spectrum shows more cross-term perturbation character because $E_{N_1L_1,N'L'}$ becomes smaller.

B. The shake-off process

An important extension for the shake-up process is the shake-off process, where the outer electron is shaken into a continuum orbit. Previous descriptions for the shake-off pro-

cess of $|N_1L_1\epsilon l\rangle$ frequently assumed $l=l_0$ as an extension of the overlap formula, which seems contradictory to the well known tendency that the escaped electron increases its angular momentum. Indeed, for the monopole perturbation case, $l\equiv l_0$. For higher-pole perturbations, it is not always satisfied. Here we will present numerical examples to study the effects of the higher-pole perturbations in the shake-off process of $|N_1L_1\epsilon l\rangle$ for an atomic system without penetration.

Similarly to the shake-up process, the shake-off process is due to the perturbations of the quadrupole term or/and the dipole cross term. Three possibilities for l are l_0-2, l_0, l_0+2. The shake-off process to l_0-2 is negligible compared to the other processes. The ratio of the probabilities to l_0+2 and l_0 can be expressed as

$$y_q=\frac{P^q_{l_0+2}}{P^q_{l_0}}=\left|B_q\frac{\langle n_0l_0|1/r^3|\epsilon(l_0+2)\rangle}{\langle n_0l_0|1/r^3|\epsilon l_0\rangle}\right|^2 \tag{21}$$

for the quadrupole perturbation and

$$y_{dd}=\frac{P^{dd}_{l_0+2}}{P^{dd}_{l_0}}\simeq\left|B_{dd}\frac{\langle n_0l_0|1/r^4|\epsilon(l_0+2)\rangle}{\langle n_0l_0|1/r^4|\epsilon l_0\rangle}\right|^2 \tag{22}$$

for the cross-term perturbation, where B_q and B_{dd} are the ratios of the angular momentum coupling coefficients and usually have the orders of 1. A similar approximation as in Eq. (19) has been made for y_{dd}. It should be noted that for $L_1=0$, there is no quadrupole interaction. The shake-off process to $|NL\epsilon l\rangle$ with $L\neq L_1$ can be treated in a similar way.

Figure 3 shows calculated y_q and y_{dd} based on the formula given by Nikitin and Ostrovsky [12] for $n_0=16$ and different l as a function of ϵ with the approximations of $B_q\approx 1$ and $B_{dd}\approx 1$. Both y_q and y_{dd} increase with increasing l or ϵ for the energy range shown in Fig. 3. It is evident that for high-l or high escape energy states, the escape electron in the shake-off process prefers to have an angular momentum of l_0+2. By comparing y_q and y_{dd}, it can be seen that the quadrupole perturbation, compared to the cross-term perturbation, is more likely to increase the angular momentum of the escape electron. Similarly to the shake-up process, a real shake-off process for a nonpenetrating system is a result of the constructive or destructive interference of the two perturbations.

IV. CONCLUSION

The above discussion has provided a convenient way to predict the excitation structure in the shake-up process for atomic doubly excited asymmetric states with weak electronic correlation. By revealing analytically the quantitative intrinsic relations between the overlap formula and the electronic correlation, it is shown that the overlap spectrum and the abnormal spectrum can be described quantitatively by the same theoretical framework. The criteria for applying the overlap formula are given quantitatively. In the cases of strong electronic correlation, we expect that those criteria still hold.

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