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Calculation of dissociating autoionizing states using the block diagonalization method: Application to N_2H

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Abstract. We report the calculation of preliminary potential surfaces necessary to treat dissociative recombination (DR) of electrons with N_2H^+. We performed multi-reference, configuration interaction calculations with a large active space for N_2H^+ and N_2H, using the GAMESS electronic structure code. Rydberg-valence coupling is strong in N_2H, and a systematic procedure is desirable to isolate the appropriate dissociating, autoionizing states. We used the block diagonalization method, which requires only modest additional effort beyond the standard methodology. We treated both linear and bent geometries of the molecules, with N_2 fixed at its equilibrium separation. The results indicate that the crossing between the dissociating neutral curve and the initial ion potential is not favorably located, suggesting that the direct mechanism for DR will be small. Dynamics calculations using the multi-configuration, time-dependent Hartree (MCTDH) method confirm this conclusion.

1. Introduction

Although nitrogen is very important in the chemistry of the interstellar medium, it cannot be directly observed. Its abundance must be inferred indirectly by detecting N_2H^+, which can be produced by the reaction

$$N_2 + H_3^+ \rightarrow N_2H^+ + H_2. \tag{1}$$

It was long asssumed that the N_2 consumed in the reaction above was almost completely recovered by dissociative recombination (DR). The measurements of Adams *et al* [1] in 1990 indicated that the branching ratios in the dissociative recombination process strongly favor the $N_2 + H$ channel:

$$e^- + N_2H^+ \rightarrow \begin{cases} N_2 + H \\ NH + N. \end{cases} \tag{2}$$

However, in 2004 Geppert *et al* [2] reported measurements that the branching ratio to the $NH + N$ channel was dominant. This unexpected result cast doubt on the assumptions mentioned above and motivated additional experimental and theoretical work.

In 2007, Molek *et al* [3] reported a new experimental measurement of the branching ratio and concluded that the upper limit for the branching ratio to the NH + N channel was 5%. Also in 2007, Talbi [4] reported a theoretical investigation of the potential surfaces for linear N_2H and N_2H^+. She concluded that the likely outcome of dissociative recombination would be the $N_2 + H$ channel, with N_2 in the first electronically excited state. There is now general agreement that the branching ratio to the NH + N channel is less than about 5% [5].

Talbi's work [4, 6] has highlighted the need for further calculations to determine appropriate diabatic potential surfaces for both linear and bent geometries of the molecule. This work reports preliminary calculations of that type.

2. What is needed for a DR calculation

A detailed calculation of dissociative recombination must provide potential curves for both the initial molecular ion and the dissociating autoionizing state. The surfaces needed are illustrated in figures 1 and 2. Calculating the potential surface for the initial molecular ion (N_2H^+ in the present case) is straightforward and involves standard techniques of quantum chemistry. However, calculating the dissociating state is much more difficult because that state is embedded in the continuum of scattering states that correspond to $e^- + N_2H^+$.

Recent work by ourselves [7, 8] and others [9, 10] has shown that the block diagonalization method provides a very powerful technique to determine the necessary dissociating, autoionizing states of N_2H. The block diagonalization method also allows us to determine the autoionization width Γ, which is related to the probablity that the electron incident on the molecular ion is captured into the dissociating state.

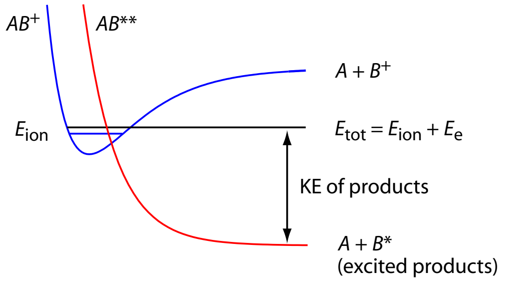

Figure 1. Potential surfaces for the molecular ion and the dissociating neutral state needed for the "direct mechanism" of DR.

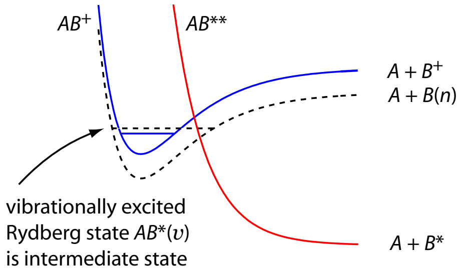

Figure 2. Additional potential surfaces for excited states of the neutral molecule are needed to treat "indirect" process for DR.

The principal difficulty that one encounters when trying to calculate the dissociating surface using the standard techniques of electronic structure is that the states of interest are (1) highly excited and (2) strongly mixed with other states. Multiple curve crossings occur, and it can be very difficult to isolate the desired potential surface. Before going into the details of our calculations, we will present an overview of the results that can be obtained by using the block diagonalization method to separate the desired states from the many other states that appear in a standard calculation.

Figure 3 shows the standard adiabatic curves obtained, and figure 4 shows the corresponding diabatic curves. These calculations were performed in the linear geometry, and R_d is the distance from the hydrogen atom H to the center of mass of the N_2. The adiabatic curves exhibit multiple curve crossings; diabatization allows us to identify the appropriate dissociation channels.

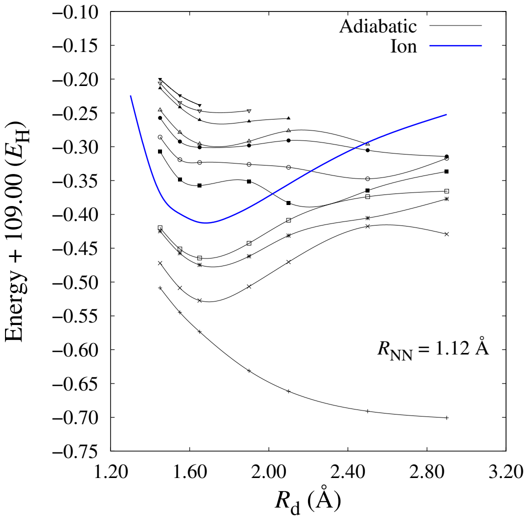

Figure 3. Adiabatic potentials determined from the GAMESS electronic structure calculations without any additional analysis.

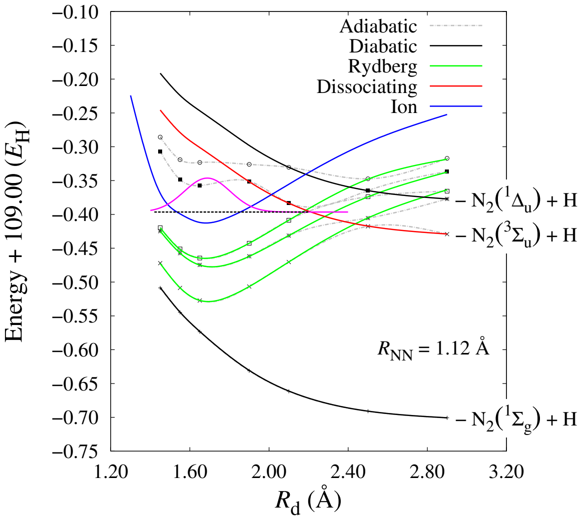

Figure 4. Diabatic potentials determined using the block diagonalization method. A vibrational wave function for the ion is also shown.

3. Block diagonalization method

The block diagonalization method [9] provides an effective technique for transforming the results of a standard electronic structure calculation into diabatic potential curves. An advantage of the method is that one can perform a conventional calculation of the desired size and accuracy and then obtain diabatic curves with comparable reliability. A second advantage is that the numerical effort for the diabatization is quite modest compared to the original calculation (which usually involves diagonalizing a very large, sparse matrix.)

The method requires extra effort in the determination of molecular orbitals (mo's). Briefly, one must insure that the variation of the mo's $\{\phi_i\}$ with molecular geometry is small. This result can be achieved by setting up the calculation in such a way that the adiabatic energies are invariant under a rotation of certain molecular orbitals, and then selecting an appropriate rotation at each geometry. For example, the MCSCF energies are invariant under an arbitary rotation $\mathbf{U}$ of the mo's in the active space [11, 12]. One can replace a set of orbitals $\{\phi'_i\}$ optimized in an MCSCF with a new set

$$\phi_i = \sum_j U_{ij}\phi'_j, \tag{3}$$

and the MCSCF energies will not change. [9] pointed out that one can take advantage of this degree of freedom by choosing $\mathbf{U}$ so that each mo in the set $\{\phi_i\}$ resembles as closely as possible a corresponding orbital in a set of "reference" orbitals. The reference orbitals are defined in a way that makes them easy to interpret and insures that they are slowly varying. We use the algorithm we previously implemented [7] based on a series of Jacobi rotations to maximize the overlap of each ϕ_i with the corresponding reference orbital.

The configuration interaction (CI) electronic wave function Ψ_n for the n^{th} state is represented as the sum of configurations Φ_m, each constructed from the mo's ϕ_i:

$$\Psi_n = \sum_{m=1}^{N} c_{mn}\Phi_m, \tag{4}$$

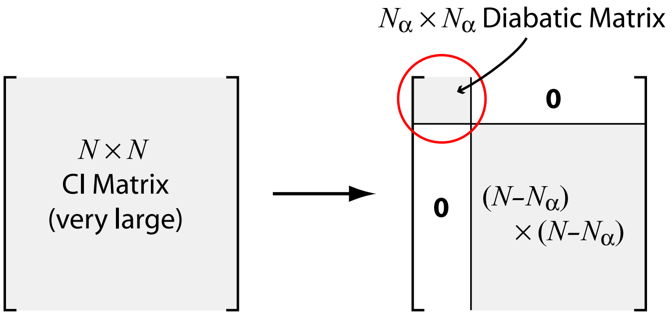

Figure 5. Schematic illustration of block diagonalization. The $N_\alpha \times N_\alpha$ block of interest can be found by applying the transformation **T** to the diagonal matrix **E** according to Eq. (5). The larger block of size $N - N_\alpha$ need not be explicitly determined.

The number of coefficients N in the sum in Eq. 4 may be quite large (of order 10^6). However, one can usually identify a small set of N_α configurations ($N_\alpha \sim 2$–10) that make the dominant contribution to N_α electronic states of interest. Then N_α will be the dimension of the diabatic Hamiltonian, and for the diabatization one only needs the $N_\alpha \times N_\alpha$ matrix of values c_{mn} for the coefficients of the N_α dominant configurations in the N_α states of interest. We denote this matrix by **S**. The diabatic Hamiltonian matrix $\mathbf{H}_{\text{dia}}$ can be expressed as a transformation of the diagonal matrix **E** whose nonzero elements are the adiabatic eigenvalues $E_1, \ldots, E_{N_\alpha}$:

$$\mathbf{H}_{\text{dia}} = \mathbf{T}^\dagger \mathbf{E} \mathbf{T}, \tag{5}$$

where (†) denotes the adjoint (transpose for a real transformation), and

$$\mathbf{T} = \mathbf{S}^{-1} \left(\mathbf{S}\mathbf{S}^\dagger \right)^{1/2}. \tag{6}$$

This analysis of the adiabatic eigenvalues and eigenvectors is straightforward and only involves matrices of order N_α. Since $\mathbf{H}_{\text{dia}}$ is explicitly constructed by a unitary transformation of the matrix **E** of adiabatic eigenvalues, the eigenvalues of the small matrix $\mathbf{H}_{\text{dia}}$ will be exactly the same as the chosen N_α eigenvalues of the large matrix determined by the CI calculation. The determination of $\mathbf{H}_{\text{dia}}$ is illustrated schematically in figure 5.

4. Electronic structure calculations

The electronic structure calculations reported here were performed using the GAMESS code [13]. The basis set included a 6-311$G(d,p)$ on each N plus diffuse functions and a $10s4p1d$ basis on H; there were 69 total basis functions. Using the notation of Talbi [4] for the molecular orbitals, the orbital occupancy of the ground state of N_2H^+ is

$$1s_a^2\, 1s_b^2\, (NN)^2\, (SP)^2\, (NH)^2\, \pi_x^2\, \pi_y^2 \Big|,$$

where the vertical bar $\Big(\Big| \Big)$ signifies the highest orbital occupied in the ion core. The orbital occupancy of the N_2H ground state is

$$1s_a^2\, 1s_b^2\, (NN)^2\, (SP)^2\, (NH)^2\, \pi_x^2\, \pi_y^2 \Big| (NH^*)^1.$$

The Rydberg states of N_2H have one electron in a highly excited orbital outside of the ion core:

$$1s_a^2\, 1s_b^2\, (NN)^2\, (SP)^2\, (NH)^2\, \pi_x^2\, \pi_y^2 \Big| (NH^*)\, \pi_x^*\, \pi_y^*\, (NN^*)\, (\text{Ryd}\,1)^1\, (\text{Ryd}\,2)\, (\text{Ryd}\,3) \ldots;$$

we use a light color to indicate that orbitals such as (NH^*) are not occupied. The dissociating valence states of N_2H have an unoccupied core orbital:

$$1s_a^2\, 1s_b^2\, (NN)^2\, (SP)^2\, (NH)^2\, \pi_x\, \pi_y^2 \Big| (NH^*)^1\, \pi_x^{*\,1}\, \pi_y^{*\,1}$$

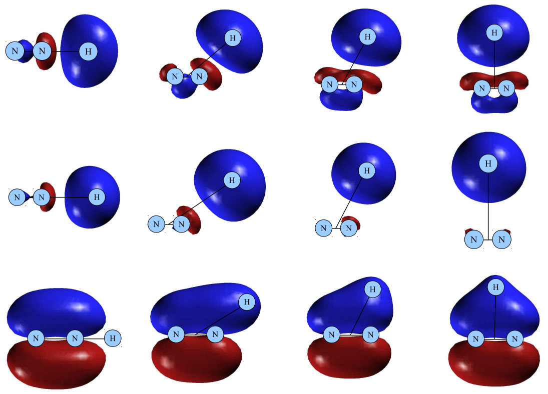

Figure 6. Variation of the molecular orbitals with molecular geometry. The top row shows the antibonding NH* orbital for $R_{\mathrm{d}} = 1.61$ Å, and $\theta = 0$, 30, 60, and 90 degrees. The second row shows the same orbtial for $R_{\mathrm{d}} = 2.46$ Å, at the same angles. The third row shows the A' bonding π orbital for $R_{\mathrm{d}} = 1.61$ Å, and $\theta =$ 0, 30, 60, and 90 degrees. The smooth changes in the molecular orbitals ensure that the block diagonalization process gives reliable diabatic potential curves.

$$1s_a^2\, 1s_b^2\, (NN)^2\, (SP)^2\, (NH)^2\, \pi_x^2\, \pi_y \,\big|\, (NH^*)^1\, \pi_x^{*\,1}\, \pi_y^{*\,1}$$

The dissociating state important for DR is a linear combination of states corresponding to the two orbital occupancies given above.

We have completed multi-reference, configuration interaction (MRCI) calculations with an active space that includes the (NH), π_x, π_y, NH*, π_x^*, and π_y^* orbitals. We included single and double excitations from the active space, leading to 449,892 configurations. We typically calculated 25-85 eigenvalues and eigenvectors of the electronic Hamiltonian. These results are preliminary; final calculations will use a larger active space that includes Rydberg orbitals.

An important requirement for the block diagonal method is that the molecular orbitals vary smoothly with geometry. For most of the calculations reported here, it was sufficient to use natural orbitals determined by a preliminary CI calculation on the N_2H ground state. These orbitals can be determined by the GAMESS code. It was necessary to watch for "orbital swaps." GAMESS orders the molecular orbitals according to an orbital energy; this procedure can lead to an unwanted interchange of two or more orbitals as the geometry changes. By estimating the orbital overlap between corresponding orbitals at similar geometries we were able to reorder the orbitals as necessary. In a few cases, such as small values of R_{d}, it was necessary to define reference orbitals explicitly as described in section 3. Figure 6 illustrates the smooth variation of the orbitals we used.

We primarily investigated the case in which DR leads to breaking the NH bond, so we froze the NN bond length at the equilibrium value appropriate for N_2H (taken to be $R_{\mathrm{NN}} = 1.12$ Å). For this case it is convenient to use Jacobi corrdinates, which are illustrated in figure 7. R_{d} is the distance from the H atom to the center of mass of the N_2, and θ is the bending angle ($\theta = 0$ corresponds to a linear molecule.) One can then expand the potential surface using Legendre polynomials of even order:

$$V(R_{\mathrm{NN}}, R_{\mathrm{d}}, \theta) = \sum_{\lambda(\mathrm{even})}^{2N} V_\lambda(R_{\mathrm{NN}}, R_{\mathrm{d}}) P_\lambda(\cos\theta) \tag{7}$$

We typically performed calculations for 8–11 different angles at each value of R_{d}. The calculated points are shown in figure 7. We have plotted the points as functions of $\sin^2\theta = 1 - \cos^2\theta$ in order to facilitate least squares fitting. A Legendre polynomial expansion with only even terms for $\lambda = 0, \ldots, 2N$ is an N^{th} degree polynomial in $\cos^2\theta$ or, equivalently, in $\sin^2\theta$. By plotting the calculated points vs. $\sin^2\theta$ we could assess the goodness of fit using standard polynomial fitting routines.

The curves shown in figure 7 are typically five-term polynomials (in $\sin^2\theta$). It is clear from these curves that an exact fit to the calculated points would have additional undulations. We

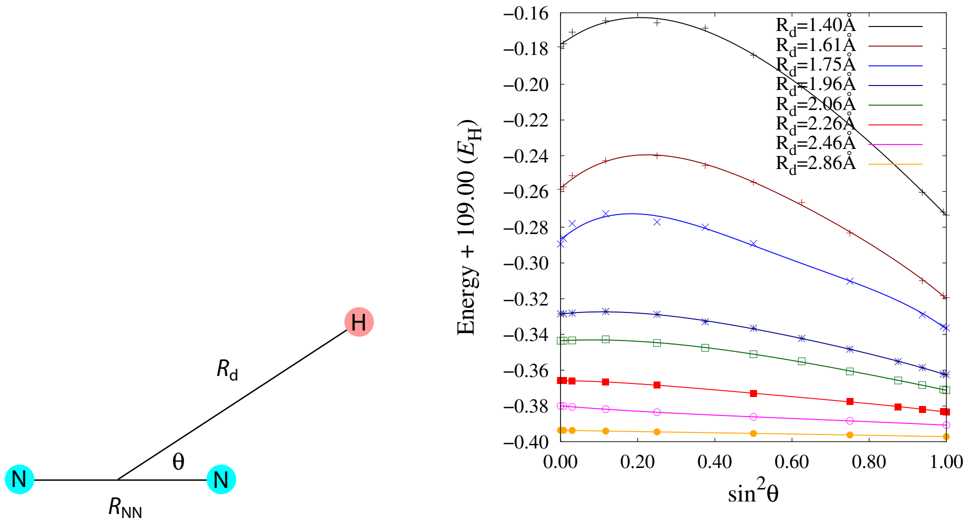

Figure 7. The left panel illustrates Jacobi coordinates. The right panel shows the angular dependence of dissociating potential. Calculated points and a five-term polynomial fit are shown.

prefer to have a somewhat smoother fit, because the additional variation in the calculated points is likely due to the uncertainty is selecting the optimum N_α and the most important configurations for each geometry. Because of the many curve crossings, the set of configurations that make the most important contribution is constantly changing. Note that the points most distant from the fitted curve tend to be at small values of R_d, where the potential is the steepest and small uncertainties are unlikely to be important.

Once the Legendre polynomial expansion coefficients in Eq. (7) have been determined for several values of R_d, they can easily be interpolated using splines. (R_NN is fixed.) Then the full surface can be interpolated at arbitrary values of R_d and θ. The interpolated results are shown in figures 8 and 9. For both of these figures, we have plotted the energy vs. the cartesian coordinates of the H atom in the plane of the molecule ($x = R_\mathrm{d}\cos\theta$ and $y = R_\mathrm{d}\sin\theta$).

5. Dynamics calculations

We have performed preliminary dynamics calculations using the multi-configuration, time-dependent Hartree (MCTDH) method [14]. This method has emerged over the past few years as a very efficient procedure for numerical solutions of the time-dependent Schroedinger

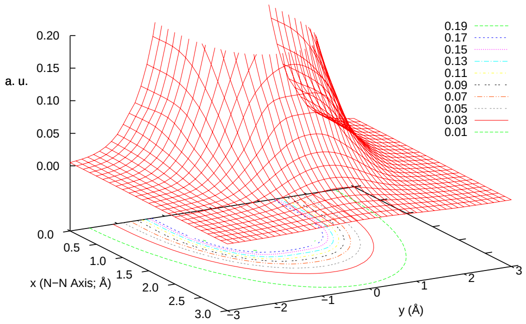

Figure 8. Surface plot of the lowest autoionizing dissociating state of N_2H.

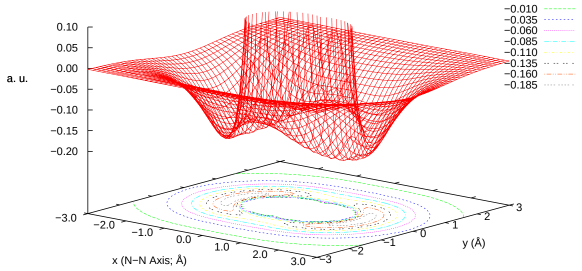

Figure 9. Surface plot of the ground state of N_2H^+.

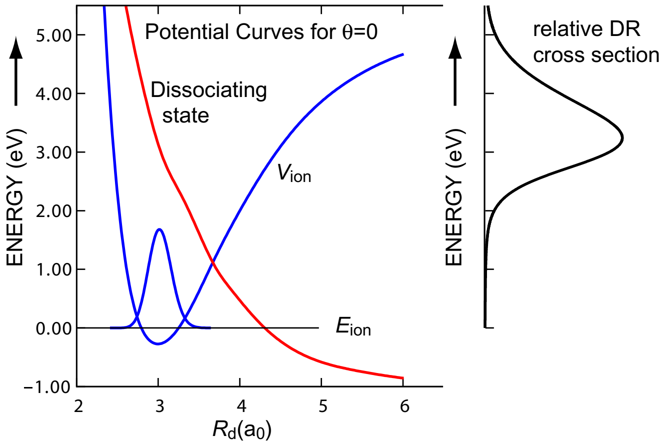

Figure 10. Potential curves for N_2H^+ and N_2H and relative cross sections for DR calculated using the MCTDH method. The dynamics calculations include the angular dependence of the potential surface but only the direct mechanism for DR. The energy scale is the same for both panels; the peak of the DR cross section occurs near an incident electron energy of 3 eV. The cross section from the direct mechanism for very low electron energies is very small.

equation. The MCTDH code permits the solution of the Schroedinger equation at various levels of accuracy; for our relatively small (triatomic) molecules, we were able to use the methods that provide an essentially exact solution.

The potential surfaces shown in figure 10 for the linear molecule ($\theta = 0$) demonstrate that the Franck-Condon factors between the vibrational ground state of N_2H^+ and the N_2–H scattering states are poor. However, as the molecule bends, the crossing between the dissociating potential and the ion potential moves to smaller values of R_d. Since the zero point motion of the molecular ion leads to a distribution of bending angles, it seemed possible that direct DR might occur. We performed dynamics calculations to investigate this possibility

Since we do not yet have the autoionization width, we performed the DR calculations using a model with simplifying assumptions (which can be avoided in future work). We used the built-in capability of the MCTDH code to treat photodissociation; if one assumes that the Γ is small and constant the processes are formally very similar. A small value of Γ corresponds to assuming that the survival factor is unity, a constant Γ is essentially an unknown multiplicative constant, so at this point we can only determine the relative cross section.

Using the full angular dependence of the potential surface we calculated for N_2H^+, we first determined the ground state wave function for N_2H^+. Then we used that wave function as the initial condition (the wave function at $t = 0$) for propagation on the dissociating surface. The relative DR cross sections we determined are presented in figure 10. The peak of the calculated cross sections occurs for an incident electron energy of about 3 eV; the value for low energy electrons (300 K or lower) is clearly very much less. The figure also shows (on the same energy scale) the ionic and dissociating potential curves; it is clear that the peak of the DR cross section occurs near the energy where the Franck-Condon factor between the initial vibrational wave function and the final scattering state is the largest. The conclusion seems clear that for any reasonable value of Γ, the absolute cross section (for direct DR) for low-energy electrons will be very small.

6. Concluding remarks

We have reported preliminary large scale electronic structure calculations for the ground state of N_2H^+ and for several states of N_2H, including the dissociating state important for dissociative recombination. Initial dynamics calculations that include the bending of the molecule but freeze the N_2 bond length suggest that the direct mechanism of DR is not efficient. Further work is needed for a definitive calculation.

Acknowledgments

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