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ELECTRONIC STRUCTURE OF CONJUGATED POLYMERS effective Hamiltonian metodo Vent (0) par also been used to obtin in cather one electron orbitals for bolymers with "http: complete time and excession

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Department of Chemistry, M.I.T., Cambridge, MA 02139 USA by parameters (or in some cases, unclined chosen in that the

Pariser-Parc-Pole (PPP), CNDO, NHDO, er. (7), Stoce the first In this paper, I will review recent work on certain aspects of the electronic structure of conjugated polymers, and try to make contact with the work on the electronic structure of short oligomers. It is impossible to cover this vast subject except by ignoring a great deal. I therefore do not pretend to be exhaustive; instead I will cover a few topics of current concern and hope that these overlap sufficiently with the interests of people studying the properties of polydiacetylenes. limbed together with the nuclear pocential to form a

# 1 THE QUANTUM CHEMISTRY OF CONJUGATED SYSTEMS

First, I will briefly remind you of the standard methods for finding approximate wave functions for the states of conjugated molecules (1). We work in the Born-Oppenheimer approximation always, so that we fix the nuclear positions and write the H =  $\Sigma \{-\frac{1}{2}\nabla_i^2 - \Sigma \frac{Z_n}{r_{in}} + \frac{1}{2}\Sigma \frac{1}{j \neq i}\} + \Sigma \frac{Z_n Z_m}{r_{nm}}$ electronic Hamiltonian as

where  $Z_n$  is the charge on the nth nucleus,  $r_n$  is the position of that nucleus and r; is the position of the ith electron. Of course, the Schrodinger equation cannot be solved for such a Hamiltonian if there is more than one electron, so we must resort to approximate methods. The usual first approximation is to assume that the electrons are each in one-electron orbitals which are solutions to the Hartree Fock (HF) equations (2). These treat each electron in the average field of all the other electrons, and

yield one electron orbitals and energies. The HF approximation is often very good, especially for ground state closed shell systems. To go beyond HF, one must use multiconfigurational methods (3) or generalized valence bond methods<sup>4</sup> or pseudopotentials plus density functional methods (5). All these methods are time consuming and expensive and have not yet been applied to many polymeric systems.

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In recent years, a pseudopotential-like method, the valence effective Hamiltonian method (VEH) (6) has also been used to obtain HF-caliber one electron orbitals for polymers with little computer time and expense.

Because all the ab-initio methods mentioned above are quite time consuming, <u>semi-empirical</u> methods have been developed which replace certain integrals appearing in the Hartree Fock equations by parameters (or in some cases, functions) chosen so that the results fit the spectral properties of certain model compounds. Some of these methods are the Huckel model, Hubbard model, Pariser-Parr-Pople (PPP), CNDO, MNDO, ... (7). Since the first three of these methods are related and have played a significant role in he work of the last few years, I will discuss them in

The PPP model is the most complete model in this hierarchy (of Huckel, Hubbard and PPP), and it begins with the HF equations for the one electron  $\pi$ -molecular orbitals of a conjugated molecule. Only  $\pi$  orbitals are considered so all the  $\sigma$  electrons are lumped together with the nuclear potential to form a "core" Hamiltonian, hcore. Each carbon nucleus has one pz atomic orbital (for simplicity I consider planar systems), called un, n labelling the nucleus. Note that the molecular orbitals are linear coefficients in this linear combination we are trying to find. In the HF equations for the molecular orbitals there will be one electron integrals, Coulomb integrals and exchange integrals. All of these can be written as sums of integrals over atomic orbitals. The semi-empirical nature of the PPP method enters here: these integrals over atomic orbitals are parameterized by comparing the final results with the experimental results for the spectrum of benzene, for example. Thus, one electron integrals become

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 $\langle u_{n}(1) | h_{core}(1) | u_{n'}(1) \rangle \equiv \beta(r_{nn'})$ 

while two electron integrals are

 $\langle u_n(1)u_m(2)|\frac{1}{r_{12}}|u_p(1)u_q(2)\rangle = \delta_{np}\delta_{mq}\gamma(r_{nm})$ Santitonian if there is nore than one s Assume that the electrons of the state

94

The zero differential overlap (ZDO) approximation has been made here so that only two center integrals are considered. Note that

 $\gamma(0) \equiv U \neq 0$ 

 $\gamma(r) \sim \frac{1}{r}$  as  $r \rightarrow \infty$ 

The PPP model keeps all the one and two center two electron integrals, solves for the HF molecular orbitals (within these approximations) and compares the result to experiment. The Hubbard model neglects all the  $\gamma$  except  $\gamma(0)$  ( $\equiv$ U). The Huckel model neglects all the  $\gamma$  including U.

The PPP model has been found to be an excellent approximation for many small planar conjugated molecules such as benzene, naphthalene, etc. (7) A standard parameterization gives (in benzene)

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 $U \sim 11 \text{ eV}$   $\beta(\text{nearest neighbor}) \sim 2.4 \text{ eV}$  $\gamma(r) = U(1+0.6r^2)^{-1/2}$  (r in Å)

Even though the PPP model has been successful, it was recognized quite early that using single determinational wave functions was overly restrictive, and to obtain better results, configuration interaction with other determinants should be included. Karplus and co-workers (8) have used this procedure to take the PPP model further than before.

Since the Hubbard and Huckel models are approximations to the PPP model, they are bound to be less reliable. However, when used cleverly, they can be qualitative and even semi-quantitative guides to the electronic structure.

The MNDO method pioneered by Dewar (9) has proved itself to be reliable and semi-quantitative for the geometries of small organic molecules and has been used recently (10) to study the defect in polyenes, as has the PPP method (11). The results are in reasonably good agreement.

Another way of dealing with these semi-empirical methods is to write down the Hamiltonian, in operator form, after all the approximations have been made. The PPP Hamiltonian is then

 $H = \sum_{\substack{n,n \in \sigma}} \{\sum_{\substack{n,n \in \sigma}} \beta_{nn} \cdot (a_{n\sigma}^{\dagger}a_{n} \cdot \sigma + a_{n}^{\dagger} \cdot \sigma a_{n\sigma}) \}$ 

+  $\hat{n}_{n} \varepsilon_{n} \delta_{nn'}$  +  $\frac{1}{2} U_{n} \delta_{nn'} \hat{n}_{n} (\hat{n}_{n-1})$  +  $\frac{1}{2} \gamma_{nn'} (1 - \delta_{nn'}) (\hat{n}_{n-1}) (\hat{n}_{n'-1})$  $\hat{n}_n = \Sigma a_n^{\dagger} \sigma a_n \sigma$ 

and  $\sigma$  labels the spin of the electron. Once this many electron Hamiltonian has been written down, we do not have to solve the Hartree-Fock problem, but can attempt to solve the Schrodinger equation <u>exactly</u>. Recently, Soos and co-workers have attempted this within a valence bond approach (12) with good results. Note that if all the Ynn' are neglected, the standard Hubbard Hamiltonian results with its correlation parameter, U. (By the

way, the U term, although a two electron term, is contained within the standard up the standard HF approximation, so a quantum chemist would not label it a correlation term, but a Coulomb term). Note further that if U is neglected in addition to Ynn', the general Huckel

This Hamiltonian is also a useful starting point for discus-

sing electron phonon interactions. If we expand  $\beta_{nn'}$  and  $\gamma_{nn'}$ around the equilibrium geometry of the structure so that for

 $\beta_{nn'} = \beta_{nn'} + \kappa (u_n - u_{n'}) + \cdots$ where  $\kappa$  is the electron phonon coupling constant and  $u_n$  is the derivation of the other phonon coupling constant and  $u_n$  is the derivation of the nth nucleus from its equilibrium position. Fnn' and un are neglected, the Hamiltonian becomes the Su, Schrieffer, Heeger (13) (SSH) Hamiltonian when the vibrational Hamiltonian for the concerns.

Hamiltonian for the cores is added. Thus, the SSH model is identical to Huckel theory with  $\sigma$  bond elastic energy (1).

APPLICATION TO POLYENES 2

2.1 Electronic Structure for Regular Geometries The polyenes have been studied in the Huckel and PPP models ysical chemists over the lated in the Huckel and PPP models by physical chemists over the last thirty years. The early work is summarized by Salem (1). An import thirty years. summarized by Salem (1). An important question was the origin of the optical gap which persists portant question was the origin. If the optical gap which persists as the polyene becomes longer. If all the bonds were of equal longet the polyene becomes longer. If all the bonds were of equal length so that all the nearest neighbor  $\beta$ 's were equal, then which length so that all the nearest neighbor  $\beta$ 's were equal. bor B's were equal, then Huckel theory predicts that the optical gap would disappear as N the theory predicts that the even gap would disappear as N, the number of double bonds in the even polyene, goes to infinity solumber of double bonds in the even polyene, goes to infinity. Salem and Longuet-Higgins (1) noticed

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that if bond alternation were allowed, then the gap persisted as N+∞, and, in addition, the bond alternated structure had a lower total energy than the equal bond length structure. (This is an example of a Peierls instability (13).)

If within the Huckel model there are just two  $\beta$ 's,  $\beta$ long and <sup>β</sup>short, (corresponding to a fixed bond-alternated geometry) given ppp prediction (within the grow  $\beta_{\text{long}} = \beta(1+\delta)$   $\beta_{\text{short}} = \beta(1-\delta)$ by

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then the gap is given by  $\Delta E=4\beta\delta$  as N+ $\infty$ .

The optical gap for short chain polyenes was computed in the PPP model by Johnson and Peacock (14) who found that even in the equal bond case ( $\delta=0$ ), there seemed to be a gap as N+ $\infty$ .

The gap has also been computed in the Hubbard model in the equal bond length geometry by Lieb and Wu (15)who found a nonzero gap as long as  $U\neq 0$ . Thus, the optical gap can be caused solely by the electron-electron interactions. In the alternating bond structure in the Hubbard model, no exact solution is known, but a meanfield result (16) leads to a gap,  $\Delta$ ,  $\Delta = [\{\Delta(\delta=0)\}^2 + \{4\beta\delta\}^2]^{1/2}.$ 

The exact optical gap in the PPP model for an infinite bond alternated structure is not known; however, it is clear that electron interactions can play an important role in the size of the gap.

Another important question is whether single determinational functions (i.e. within the Huckel or Hartree Fock approximations) describe the lowest excited states of polyenes correctly. In the last ten years (17), it has become clear from both experiment and theory that the lowest excited state of even polyenes with more than three double bonds is not the  $B_{1u}$  state reached by the absorption of light, but a second  $A_{1g}$  state accessible by two photon absorption. Thus the Hartree Fock model, although a very good decent the second  $A_{1g}$  state accessible by two photon absorption.  $g_{00d}$  description of the  $B_{1u}$  excited state, is not good at all for the lowest excited state. At the present time, the behavior of this Alg state (and other such states) as the polyene grows longer is completely unknown, although a valence bond description of this state resembles a soliton-antisoliton pair of the SSH model, but within a rigid geometry. A saturation and the saturation with a saturation and the saturation of the saturati

defects in long polyene chains was first discussed by Pople and Walmsley (18) in 1962 Theins was first discussed by Pople and Walmsley (18) in 1962. They treated the Huckel Hamiltonian for a bond alternated (i.e. dimensional) bond alternated (i.e. dimerized) chain in which spin 1/2 defects were inserted by having the identical chain in which spin 1/2 defects were inserted by having two long (single) bonds in a row. This defect changes the phase of the single bonds in a row. defect changes the phase of the alternation. They did not allow the structure to relax around the alternation. They did not allow the structure to relax around the defect so that the domain wall was infinitely sharp. was infinitely sharp. Using values of  $\beta$  current at that time, they estimated the creation of  $\beta$  current at that time, they estimated the creation energy of Such a defect and thus the number of free spins in long rely of such a defect and thus the number of free spins in long polyene chains at room temperature. (From this they speculated on the semiconducting properties of systems.) Two important of the semiconducting properties were such systems.) Two important features of this structure were clearly recognized in the namer. clearly recognized in the paper: the defects could be pulled as far apart as one liked (i.e. decentre defects could be pulled as far apart as one liked (i.e. degenerate ground states) and the easy movement of the defect (domain unit) (domain unit) easy movement of the defect (domain wall). However, these authors did not notice that the energy gain by 11. However, these defect to did not notice that the energy gain by allowing the defect to spread was large. In 1979. Su Scheid Color ovamined spread was large. In 1979, Su, Schrieffer, and Heeger examined

As Salem (1) points out, the electronic structure of spin 1/2 ts in long polyene chains the electronic structure of spin 1/2

# 2.2 Electron-Phonon Interactions

Although the Soos work has raised important questions, it has answered others with final raised important questions, it has also answered others with finality. For example, it is now absolutely clear that to describe the states of polyenes quantitatively requires electron-electron interactions (U and Y above). If they are lost above). If they are left out, the excited state energies, spin densities in radicals of out, the excited state energies, (12) has densities in radicals, etc. are given incorrectly. Soos (12) has

Within the last year, Soos (12) has found the exact energies of the polyenes up to six double bonds within the PPP model, assuming a bond alternated geometry with  $\delta=0.07$  for the neutral molecules, and equal bond geometry for certain ions and radicals. This beautiful work is so new that the results are still being interpreted. However, I believe that Soos has opened a new era in the study of polyeror, it believe that Soos has opened a that the the study of polyenes with this breakthrough. He finds that the PPP prediction (within the geometry mentioned above) for the vertical optical gap for tetraene is 4.56 eV (expt=4.4 eV), for pentaene 4.23 eV (expt=4.0 eV), and for dodecaene 4.0 eV (expt=3.7 eV), while the prediction (ev) eV), while the prediction for the  $2A_{1g}$  vertical gap is 3.8 eV (expt 3.6 eV) and for pentaene 3.4 eV (expt=3.1 eV). An extrapola-tion to N= $\infty$  gives an optical constant of a evolution of the expt set of the expt set of the expt set of the evolution of the tion to  $N=\infty$  gives an optical gap of 2.8 eV (expt=3.1 eV). All extra do we account for this discussed of 2.8 eV (expt=1.8 eV)! How do we account for this discrepancy: (a) lack of bond alternation throughout the structure? (b) non-Franck Condon effects, i.e. relaxation of the B<sub>1</sub> state geometry? (c)  $\sigma - \pi$  interaction effects? Another important questions geometry? (c)  $\sigma - \pi$  interaction effects? Another important question: to what energy does the  $2A_{1g}$  state  $g^0$  does the  $2A_{1g}$  state  $g^0$ at infinite N? Where are the other A1g states? Can we describe them as a band of soliton anticolitor atticolitor. them as a band of soliton-antisoliton bound states?

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## this model again (13), and repaired this oversight.

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By allowing the bond alternation to change continuously through the defect and taking  $\beta(r)$  from the quantum chemists standard formulary, SSH showed that the optimized geometry was a soliton-like structure. That is, the difference in bond lengths in a unit cell varied as tanh  $(n/\ell)$  where n numbers the unit cell (n=0 at the center of the defect) and  $\ell$  is a parameter giving the width of the defect. SSH, using the Huckel model, found  $\ell=7$  for the neutral and charged solitons  $(S_0, S_+, S_-)$ . The seminal work of SSH led to an enormous interest in the theoretical description of this system.

The interaction between defects on a polyene chain were considered within the SSH model by Maki et al. (19), Bredas et al. (20) and Bishop et al. (21). The latter two groups noted that although like-charged defects do not bind together, a neutral and a charged defect will bind to form a polaron (or radical-ion) on the chain. Thus the complete SSH model must include the possible formation of polarons, and other defects (21).

Other authors have attempted to look at the effect of electron interactions (correlation) on these structures in a variety of ways. Some have added a Hubbard U term to the basic SSH Hamiltonian (22,23,24) and showed that as long as U<4,7 eV, the basic results of SSH are largely unaffected. The "true" value of U is not known with accuracy; however, it is likely to be close enough to the critical U to be disturbing. If U>4.7 eV, there is an undimerized spin density wave state which is lower in energy than the normal solution. Aslangul (24) has an interesting discussion on this. J. Fukutome and Sasai (11,25) have tried to solve the PPP Hamiltonian within the unrestricted Hartree Fock approximation, and find both SDW and CDW solutions, although the normal bond-alternated solution does seem to be the best description of the electronic structure here. As we pointed out above, Soos' (12) methods have not yet been applied to long polyenes.

Another approximate scheme, MNDO, has been applied to the study of defects (10,26) in long polyenes. This self-consistent method allows the inclusion of electron interactions in an approximate way and leads to predictions similar to those of the SSH model. For example, the neutral defect is studied by exaining a 41 carbon atom polyene with a center of symmetry. This forces the defect to be centered in the middle of the chain. The MNDO results show the standard tanh structure but with &=3 (instead of &=7 from the Huckel model). The charged defects were treated in the same manner and it was found that &=5 for the positive and &<3 for the negative solitons. Note however that the tanh form was

found in all cases. These authors also discussed the structure of the orbital which is singly occupied in the neutral defect (i.e. mid-gap orbital). The results of the MNDO calculation are in good semi-quantitative agreement with the UHF results in the PPP model (25).

In spite of their simplicity and inexact character, the application of semi-empirical Hamiltonians and methods to the electronic structure of polyenes has proven to be an extremely fertile endeavor, allowing a better understanding of experiments and giving rise to simple models of immense utility.

## 3 QUANTUM CHEMISTRY OF POLYMERS

In the past few years, the work of Ladik, Andre, Karpfen, Suhai, Kerstesz and others (27) has led the way to a greater under standing of the electronic structure of polymers. Using ab-initio methods mainly, these authors have shown that high quality electronic structure calculations can be done on polymers in the same way as on semiconductors and metals. At the same time, semiempirial methods have been applied to this problem with success. Duke et al. (28) have used CNDO methods, while Bredas et al. (29) have used valence effective Hamiltonian (VEH) methods.

The current status of ab-initio calculations on the ground state properties of polymers is given in the review by Karpfen.<sup>30</sup> The band structures and densities of states of polyacetylene (and polyethylene) are given in the crystal orbital method (Hartree Fock with periodic boundary conditions). Correlation effects have been treated by Suhai (31) in order to study the optical band gap. Although progress is surely being made in this field, the effort required per calculation is large, and it is important that approximate and semi-empirical methods be developed. One such method which has proven to be very useful is the valence effective Hamiltonian (VEH) method mentioned above. This is a method for obtaining molecular one-electron Hamiltonians from first principles and has been worked out by Nicolas and Durand (6,32). The effective Fock operator of the molecule is assumed to be the sum of the kinetic energy and the various atomic potentials in the

$$F_{eff} = -\frac{\Delta}{2} + \sum_{A} V_{A}$$

where VA is the effective potential of atom A. For computational ease, simple nonlocal atomic potentials are chosen of the form of

Gaussian projectors:

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$$V_A = \sum_{lm} \sum_{i,j} \sum_{i,j} C_{ij,lm} | x_{ilm}^A \times x_{jlm}^A |$$

where the summations over & and m define the angular dependence of  $V_A$ . The numerical coefficients  $C_{ij}$ , &m are independent of m in the case of spherical symmetry, which we usually consider. The functions are normalized Gaussians:

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#### $X_{ilm} = N_i \exp[-\alpha_i r^2] Y_{lm}(0, \phi)$

 $N_{\rm j}$  is the normalization factor and  $Y_{\ell m}$  denotes the usual spherical harmonics. Note that only 1s and 2p Gaussian Cartesian functions are used.

The parameterizations of the linear coefficients, C, and the nonlinear exponents,  $\alpha$ , first require valence SCF calculations on model molecules by a theoretical pseudopotential method with an STO-3G minimal basis set and a double zeta basis set. The model molecules chosen to parameterize carbon and hydrogen atomic poten-tials were ethane, transbutadiene, and acetylene (29); for sulfur and carbon linked to sulfur, dimethyl sulfide and thiophene (29); for ni-trogen and carbon linked to nitrogen, dimethylamine and pyrrole (33). For each molecule, the Fock operator is constructed as:

 $F = \Sigma \varepsilon_{\nu} |\phi_{\nu} > \langle \phi_{\nu} |$  and showing that another the electron tent

where the summation is over all occupied states; the valence orbitals  $\phi_{U}$  are taken from the minimal basis set calculation and the corresponding monoelectronic energies  $\varepsilon_{U}$  from the double zeta calculation. The choice of this theoretical Fock operator leads to valence effective Hamiltonians providing double zeta accuracy for monoelectronic energies when solved with a minimal set. The parameterization of the atomic potentials is then determined by minimizing the quantity

# $B^{\Sigma}$ (F-F<sub>eff</sub>|F-F<sub>eff</sub>)molecule B

where the summation runs over the model molecules used for a given set of atomic potentials. (F-Feff|F-Feff) denotes the scalar product of F-Feff with itself in the subspace of the occupied valence orbitals. On the model molecules, standard deviations between the  $\varepsilon_{0}$  energies produced by using the valence effective Hamiltonians and double zeta energies are of the order of 0.015 a.u., and in no case larger than 0.2 a.u. The position of the highest occupied orbital is especially well-produced - a result which lends confidence in obtaining good ionization potential estimates.

No information pertaining to the excited states is included in the atomic potentials. As a result, no special attention should in principle be given to the unoccupied levels. However, for the planar systems considered previously, surprisingly good agreement between experiment and theory has been obtained for the lowest optical energy transition (29).

The extension of the VEH method to polymer calculations is straightforward. The effective operator takes the form:

$$F_{eff} = -\frac{\Delta}{2} + \sum_{g} \sum_{A} V_{A}$$

the summations over g and A running, respectively, over the polymer unit cells and the atoms present in one cell. The band structure E(k) of the polymer, where k is a point in the first Brillouin zone of the polymer, is obtained from eigenvalues of the set of secular equations:

$$\underline{\underline{r}(k)} \underline{\underline{C}(k)} = \underline{\underline{S}(k)} \underline{\underline{C}(k)} E(k)$$

F(k) and S(k) are the Fock and overlap matrices between Bloch functions and C(k) collects the coefficients of the linear combinations of Block functions that provide the crystalline orbitals.

The main advantages of the VEH technique are that it is completely theoretical and gives ab-initio double zeta quality results with negligible computer time, since only one-electron integrals need to be evaluated and SCF iterative cycles are completely avoided.

It must be pointed out that the VEH atomic potentials have not been parameterized for geometry optimization purposes and should be used with geometric parameters close to equilibrium. For systems whose geometries are experimentally unknown (as is the case of the majorithe majorithe are experimentally unknown (as is the case of the majority of the large oligomers and polymers studied), we must make use of the large oligomers and polymers studied) we must make use of other techniques in order to obtain reasonable input geometries. Ab-initio techniques, even with small basis sets, rapidly become to initio techniques, even with small basis sets, rapidly become too expensive when large compounds are considered. As a result we often use geometries optimized with a method such as MNDO method such as MNDO.

The results for polyacetylene, polydiacetylenes, polyphen-

102

ylene, polypyrrole and other polymers using the VEH method have been published. A comparison between the ab-initio Hartree-Fock crystal orbital results and the VEH results on polyacetylene shows perfect agreement for minor details. It seems therefore that the VEH method is an inexpensive way to derive excellent one electron energies and wave functions for the ground state of polymers. . Budson, B. Kohler, K. Schulten, Excited Statesh vo

#### 4 CONCLUSIONS

At the present time, ab-initio Hartree-Fock and VEH methods can yield reliable ground state one electron properties. Correlation energies require more effort and are not yet available Hang, B. Campbell, K. 1855er, for many systems.

tolto and K. Matt, Plus, Key,

Semi-empirical methods (MNDO, CNDO, PPP, and its variants Hubbard and Huckel) yield semi-quantitative information on both ground and excited state properties.

With the advent of supercomputers we will soon see tremendous advances in both areas. I expect that effects of impurities and dopants, interchain effects and solid state effects will become amenable to attack using these methods in the near future.

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104