ELECTRONIC STRUCTURE OF CONJUGATED POLYMERS
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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.

## 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 electronic Hamiltonian as

$$
H=\sum_{i}\left\{-\frac{1}{2} \nabla_{i}^{2}-\sum_{n} \frac{Z_{n}}{r_{i n}}+\frac{1}{2} \sum_{j \neq i} \frac{1}{r_{i j}}\right\}+\sum_{n>m} \frac{Z_{n} Z_{m}}{r_{n m}}
$$

where $Z_{n}$ is the charge on the nth nucleus, $r_{n}$ is the position of that nucleus and $r_{i}$ 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 $H F$, one must use multiconfigurational methods (3) or generalized valence bond methods ${ }^{4}$ 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.

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, semi-empirical methods have been developed which replace certain integrals appearing in the Hartree Fock equations results fit the in some cases, functions) chosen so that the Some of these methods are the compounds. Pariser-Parr-Pople (PPP), three of these methods , CNDO, MNDO, … (7). Since the first role inthe work of the are related and have played a significant more detail.

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 molelumped toget orbitals are considered so all the o electrons are Hamiltonian, with the nuclear potential to form a "core" (for simplicity I consider carbon nucleus has one $\mathrm{p}_{\mathrm{z}}$ atomic orbital the nucleus. Note that the molecular orbitals called $u_{n}$, $n$ labelling cients in this linear combination ar orbitals are linear coeffiHF equations for the moleculation we are trying to find. In the integrals, Coulomb integrals and exbitals there will be one electron can be written as sums of int and exchange integrals. All of these semi-empirical nature of the egrals over atomic orbitals. The grals over atomic orbitals are paramed enters here: these intefinal results with the experimental benzene, for example. Thus, one elas results for the spectrum of

$$
\left\langle u_{n}(1)\right| h_{\text {core }}(1)\left|u_{n^{\prime}}(1)\right\rangle \equiv B\left(r_{n n^{\prime}}\right)
$$

while two electron integrals are

$$
\left\langle u_{n}(1) u_{m}(2)\right| \frac{1}{r_{12}}\left|u_{p}(1) u_{q}(2)\right\rangle=\delta_{n p^{\delta} \delta_{m q} \gamma\left(r_{n m}\right)}
$$

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

$$
\begin{aligned}
& Y(0) \equiv U \neq 0 \\
& Y(r)-\frac{1}{r} \text { as } r^{+\infty}
\end{aligned}
$$

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)

$$
\begin{aligned}
& U \sim 11 \mathrm{eV} \\
& \beta(\text { nearest neighbor }) \sim 2.4 \mathrm{eV} \\
& Y(r)=U\left(1+0.6 r^{2}\right)-1 / 2
\end{aligned}
$$

$$
(r \text { in } \AA)
$$

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

$$
\hat{H}=\sum_{n, n, n^{\prime} \sigma}\left(\Sigma \beta_{n n^{\prime}}\left(a_{n \sigma}^{+} a_{n} \sigma^{\prime} \sigma+a_{n}^{+} \sigma^{\prime} a_{n \sigma}\right)\right.
$$

$$
\begin{aligned}
& \left.+\hat{n}_{n} \varepsilon_{n} \delta_{n n^{\prime}}+\frac{1}{2} U_{n} \delta_{n n^{\prime}} \hat{n}_{n}\left(\hat{n}_{n}-1\right)+\frac{1}{2} \gamma_{n n^{\prime}}\left(1-\delta_{n n^{\prime}}\right)\left(\hat{n}_{n}-1\right)\left(\hat{n}_{n}{ }^{\prime}-1\right)\right\} \\
& \hat{n}_{n}=\sum_{\sigma} a_{n \sigma \alpha_{n \sigma}}^{+}
\end{aligned}
$$

and $\sigma$ labels the spin of the electro
Hamiltonian has been written ectron. Once this many electron Hartree-Fock problem, but can down, we do not have to solve the equation exactly. Recently, sompt to solve the Schrodinger this within a valence bond appros and co-workers have attempted proach (12) with good results. Hamiltonian results with $\gamma_{n n \prime}$ are neglected, the standard Hubbard way, the $U$ term, although a tworrelation parameter, U. (By the the standard HF approximation electron term, is contained within label it a correlation term, so a quantum chemist would not that if $U$ is neglected in addit a Coulomb term). Note further Hamiltonian results.

This Hamiltonian is also a useful sing electron phonon interactions. If example equilibrium geometry of the
starting point for discuswe expand $\beta_{n n^{\prime}}$ and $\gamma_{n n^{\prime}}$

$$
\beta_{n n^{\prime}}=\beta_{n n^{\prime}}^{0}+k\left(u_{n}-u_{n^{\prime}}\right)+\cdots
$$

where $\kappa$ is the electron phonon coupling constant and $u_{n}$ is the derivation of the nth nucleus from its equilibrium position. ${ }^{\mathrm{r}} \mathrm{nn}^{\prime}$ and $\mathrm{u}_{\mathrm{n}}$ are neglected, the Hamilts equilibrium becomes the Su, Hamilton, Heeger (13) (SSH) Hamiltonian becomes the Su, identical to for cores is added tonian when the vibrationa

## 2 APPLICATION TO POLYENES

### 2.1 Electronic Structure for

Regular Geometries
by physical chemists been studied in the Huckel
summarized by Salem over the last thi the Huckel and PPP models the optical gap which (1). An importantry years. The early work is all the bonds were of persists as the question was the origin of bor $\beta^{\prime}$ 's were equal, thequal length the polyene becomes longer. If gap would disappear then Huckel the that all the nearest neighpolyene, goes to infinity the numbery predicts that the optical , goes to infinity. Salem and Lof double bonds in the even
that if bond alternation were allowed, then the gap persisted as $N+\infty$, 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 $\beta^{\prime} s,{ }^{\beta}$ long and ${ }^{\beta}$ short, (corresponding to a fixed bond-alternated geometry) given by

$$
\begin{aligned}
\beta_{\text {long }} & =\beta(1+\delta) \\
\beta_{\text {short }} & =\beta(1-\delta)
\end{aligned}
$$

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 $N \rightarrow \infty$.

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 $\mathrm{U} \neq 0$. 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, $\Delta$,

$$
\Delta=\left[\{\Delta(\delta=0)\}^{2}+\{4 \beta \delta\}^{2}\right]^{1 / 2}
$$

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 $B_{1 u}$ state reached by the absorption of light, but a second $A_{1 g}$ state accessible by two photon absorption. Thus the Hartree Fock model, although a very good description of the B1u excited state, is not good at all for the lowest excited state. At the present time, the behavior of this $A_{1 g}$ 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.

Within the last year, Soos (12) has found the exact energies of the polyenes up to six double bonds within the exp model, molecules, and equal bond geometry with $\delta=0.07$ for the neutral This beautiful work is so newmetry for certain ions and radicals, interpreted. However, I new that the results are still being PPP study of polyenes with this that Soos has opened a new era in vertical ontion (within the geometreakthrough. He finds that the pentaene $\frac{0.23 \mathrm{eV}}{4.23}$ (op for tetraene is mioned above) for the eV ), while the prediction eV ), and for 4.56 eV (expt=4.4 eV), for (expt 3.6 eV ) and fiction for the $2 A^{\text {for }}$ dodecaene 4.0 eV (expt=3.7 tion to $\mathrm{N}=\infty$ gives for pentaene 3.4 eV (ertical gap is 3.8 eV we account for this optical gap of 2.8 expt $=3.1 \mathrm{eV}$ ). An extrapolathroughout the this discrepancy: (a) 2.8 eV (expt=1.8 eV)! How do relaxation of the B Another important $\mathrm{B}_{\text {lu }}$ state geometry? (c) Condon effects, i.e. at infinite $N$ ? Wuestion: to what ene (c) $\sigma-\pi$ interaction effects? them as a band of where are the other Anergy does the $2 A_{1} \mathrm{~g}$ state go Although the soos also answered others woork has raised important
absolutely clear that with finality. Fimportant questions, it has quantitatively requit to describe the for example, it is now above). If they are electron-el states of polyenes densities in radi are left out, the extron interactions ( $U$ and $r$ a careful discussion of all are given incorrectly. Soos (12) has
Sthis. $U$ and $r$
(12) hin

## 2. 2 Electron-Phonon

nteractions
defects in long polyents out, the electronic structure of spin $1 / 2$ Walmsley (18) in 1962. chains was first dic structure of spin $1 / 2$ bond alternated (i.e. diney treated the discussed by Pople and were inserted by having timerized) chain Huckel Hamiltonian for a defect changes the phas two long (sing in which spin $1 / 2$ defects the structure to relase of the alternle) bonds in a row. This was infinitely sharpax around the ternation. They did row. This they estimated sharp. Using the defect so . They did not allow number of free the creationg values of $B$ so that the domain wall (From this the spins in long energy of such a durrent at that time, such systems speculated on polyene chains a defect and thus the clearly recogniz. Two important the semicond at room temperature. far apart as easy movement of liked (i.e. Diper: the defects structure were did not notice the defect degenerate gres could be pulled as spread was larg that the energomain wall) ground states) and the spread was large. In 1979, Su gain by all. However, these authors Su, Schrieffer, and Heeger examined
this model again (13), and repaired this oversight.
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 $\mathrm{U}<4,7 \mathrm{eV}$, 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 $U>4.7 \mathrm{eV}$, 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 $\ell=3$ (instead of $\ell=7$ from the Huckel model). The charged defects were treated in the same manner and it was found that $\ell=5$ for the positive and $\ell<3$ 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. ${ }^{30}$ The band structures and densities of states of polyacetylene (and Fock with periodic boundary conditions) orbital method (Hartree been treated by Suhai (31) in order to studyrelation effects have Although progress is surely being made study the optical band gap. required per calculation is large, and in this field, the effort approximate and semi-empirical metho it is important that method which has proven to be very useful developed. One such Hamiltonian (VEH) method mentioned useful is the valence effective obtaining molecular one-eloloned above. This is a method for principles and has been worked Hamiltonians from first The effective Fock operator of out by Nicolas and Durand $(6,32)$. sum of the kinetic energy and the molecule is assumed to be the molecule: $\quad$ and the various atomic potentials in the

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

where $V_{A}$ is the effective potential of atom $A_{\text {. For computational }}$

Gaussian projectors:

$$
V_{A}=\sum_{\ell m}^{\sum} \sum_{i j} C_{i j, \ell m}\left|x_{i \ell m}^{A}\right\rangle\left\langle x_{j \ell m}^{A}\right|
$$

where the summations over $\ell$ and $m$ define the angular dependence of $V_{A}$. The numerical coefficients $C_{i j}, \ell m$ are independent of $m$ in the case of spherical symmetry, which we usually consider. The functions are normalized Gaussians:

$$
x_{i \ell m}=N_{i} \exp \left[-\alpha_{i} r^{2}\right] \gamma_{\ell m}(0, \phi)
$$

$N_{i}$ is the normalization factor and $Y_{\ell m}$ denotes the usual spherical harmonics. Note that only 1 s and $2 p$ 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:

$$
F=\sum_{\nu} \varepsilon_{\nu}\left|\phi_{\nu}\right\rangle\left\langle\phi_{\nu}\right|
$$

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

$$
{ }_{B}^{\Sigma}\left(F-F_{\text {eff }} \mid F-F_{\text {eff }}\right)_{\text {molecule }} B
$$

Where the summation runs over the model molecules used for a given Set of atomic potentials. ( $F-F_{e f f} \mid F-F_{e f f}$ ) denotes the scalar product of $F-F_{\text {eff }}$ with itself in the subspace of the occupied valence orbitals. On the model molecules, standard deviations between the $\varepsilon_{u}$ energies produced by using the valence effective Hamiltonians and double zeta energies are of the order of $0.015 \mathrm{a} . \mathrm{u}_{0}$., 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:

$$
F_{e f f}=-\frac{\Delta}{2}+\sum_{g} \sum_{A} v_{A}
$$

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:

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

$\frac{F}{f}(k)$ 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 Fhould be used with geometric parameters close to equilibrium. case of the majority of the are experimentally unknown (as is the we must make use of other targe oligomers and polymers studied), input geometries. Ab-initichniques in order to obtain reasonable sets, rapidly become Ab-initio techniques, even with small basis considered. As a result we expensive when large compounds are method such as MNDO

[^0]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.

## 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 for many systems.

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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[^0]:    The results for polyacetylene, polydiacetylenes, polyphen-

