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Ab initio effective Hamiltonian study of the electronic properties of conjugated polymers

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The valence effective Hamiltonian technique is applied to a series of polymers to compute ionization potentials, bandwidths, and band gaps. The polymers considered represent systems of interest to the conducting polymers area and include various derivatives of polyacetylene and polyphenylene, polydiacetylene, polyacene, polybenzyl, and polyyne. The theoretical results for relative ionization potentials are in excellent agreement with available experimental estimates, as well as with the observed behavior of the electrical conductivity of these systems on exposure to weak (I_2) versus strong (AsF_5) electron acceptors. The bandwidths of the highest occupied band show a qualitative correlation to the conductivities achieved with acceptor doping. Band gaps for the planar systems considered are also in good agreement with experiment.

I. INTRODUCTION

Conducting polymers are the subject of major research activity around the world. This interest initiates from the discovery that the conductivity of intrinsically insulating organic polymers, such as polyacetylene,[1] poly(*p*-phenylene),[2] poly(*p*-phenylene sulfide),[3,4] and polypyrrole,[5] can be enhanced by 10 to 18 orders of magnitude up to metallic or near metallic levels. This conductivity increase is obtained via doping with electron acceptors, such as I_2 or AsF_5, or electron donors, such as the alkali metals. Interest, both academic and industrial, has further increased by recent successful demonstration of rechargeable batteries based on doped polyacetylene.[6]

Many fundamental aspects of the electronic and structural properties of the highly conducting polymers are, however, not well established and theoretical understanding lags behind the rapid experimental developments. The reason for the latter is that doped organic polymers represent rather complicated systems whose properties are expected to be significantly affected by factors such as disorder, low dimensionality of electronic motion, and strong electron–phonon coupling.[7,8] However, accurate calculations are feasible on the ground state properties of the undoped polymers. Such calculations can aid in rationalizing the experimental results which have been gathered through efforts to dope numerous organic polymers, as well as predict new candidates for the next generation of polymeric conductors.

It has been demonstrated that a good insight into the ground state properties of polymeric systems can be obtained by quantum chemical calculations.[9] However, the SCF (self-consistent field) *ab initio* Hartree–Fock techniques, which have proved very successful on molecules, become almost prohibitively expensive when applied to polymers of interest. Cheaper semiempirical techniques could in principle be used, but are generally less reliable.

Recently, Nicolas and Durand[10] have developed an interesting approach, based on the use of valence effective Hamiltonians (VEH). Applied to hydrocarbon molecules,[10] the VEH technique affords one-electron energy levels of *ab initio* double zeta quality, at a cost comparable to semiempirical techniques such as Extended Hückel. The VEH model has recently been applied to polymer calculations.[11,12] It has been shown,[12] through calculations on polyacetylene and polydiacetylene, that the polymer VEH method also provides *ab initio* double zeta quality results for band structure and density of states. Perhaps more important with regard to the conducting polymers area, the VEH technique provides reliable ionization potentials and bandwidths, which are of prime importance in the acceptor doping process. The ionization potential determines whether a particular acceptor is capable of ionizing (or partially ionizing) the polymer. The bandwidth of the highest occupied band provides a measure of the extent of the delocalization in the system and can be roughly correlated with the mobilities of the charge carriers in that band. Thus, bandwidths of the highest occupied band should show a qualitative correlation to conductivities achieved in similar polymers upon acceptor doping. However, caution is needed because of the demonstrated inadequacy of a rigid band model to explain the properties of highly conducting doped polymers.[8]

In this paper, we report VEH calculations for a wide range of hydrocarbon polymers in order to provide a systematic and theoretically consistent description of the valence electronic properties of systems of interest in the conducting polymers area. In particular, we consider various derivatives of polyacetylene and polyphenylene, polydiacetylene, polyacene, polybenzyl, and polyyne ("linear carbon"). Band gaps for the planar systems considered are also computed and are found to be in good agreement with available experimental data.

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Section II is devoted to a brief description of the polymer VEH method. In Sec. III, we present and discuss the results obtained on the hydrocarbon polymers cited above. Conclusions of this work are given in Sec. IV.

II. VALENCE EFFECTIVE HAMILTONIAN TECHNIQUE FOR POLYMERS

The complete methodology for obtaining molecular one-electron effective Hamiltonians from first principles has been developed in Ref. 10 and has been extended for polymer systems in Refs. 11 and 12. For the sake of completeness of this paper, we briefly describe the main concepts of the method.

In the LCAO theory of polymers, the crystalline one-electron orbitals $\Psi(k)$ are expressed as linear combinations of Bloch functions $\varphi(k)$, where k is a point in the first Brillouin zone of the polymer. The band structure $E(k)$ is obtained as eigenvalues of the set of secular equations:

$$\mathbf{F}(k)\,\mathbf{C}(k) = \mathbf{S}(k)\,\mathbf{C}(k)\,E(k) \quad . \tag{1}$$

The matrices $F(k)$ and $S(k)$ are the Fock and overlap matrices between Bloch functions, constructed from atomic orbitals (usually cast in Gaussian form):

$$F_{pq}(k) = \int \varphi_p(k)\, h \varphi_q(k)\, dv = \sum_j e^{ikja} F^j_{pq} \quad , \tag{2}$$

$$S_{pq}(k) = \int \varphi^*_p(k)\, \varphi_q(k)\, dv = \sum_j e^{ikja} S^j_{pq} \quad . \tag{3}$$

The summation over j extends over all the unit cells; h is a one-electron operator; a indicates the length of the polymer unit cell; F^j_{pq} and S^j_{pq} are matrix elements respectively of the one-electron operator and the unity operator, between the atomic orbital χ_p centered in the origin unit cell and the atomic orbital χ_q centered in cell j; the matrix C collects the coefficients of the linear combinations.

In the VEH model, h is assumed to be the sum of the kinetic term and the various atomic potentials in the system:

$$h = -\frac{\Delta}{2} + \sum_g \sum_A V_A(g) \quad , \tag{4}$$

where the summations over g and A extend respectively over the polymer unit cells and the atoms present in one cell. V_A represents the atomic potential of atom A. For computational reasons simple nonlocal atomic potentials are chosen of the form

$$V_A = \sum_l \sum_m \sum_{i,j} D^A_{ij,lm} \,|\, \chi^A_{ilm} \rangle \langle \chi^A_{jlm} \,| \quad . \tag{5}$$

The summations over l and m define the angular dependence of V_A. The χ_{ilm}'s are normalized Gaussian functions. The matrix elements F^j_{pq} are now written as

$$F^j_{pq} = \langle \chi_p | T | \chi^j_q \rangle + \sum_g \sum_A \sum_l \sum_m \sum_{t,u} D^A_{tu,lm} \langle \chi_p | \chi^{Ag}_{tlm} \rangle \langle \chi^{Ag}_{ulm} | \chi^j_q \rangle \quad . \tag{6}$$

This expression has excellent convergence properties. The parameters of universal atomic potentials V_A for carbon and hydrogen have been obtained in Ref. 12. These potentials have been constructed to yield valence effective Hamiltonians [Eq. (4)] which provide one-electron energies of Hartree–Fock *ab initio* double zeta quality when solved within a minimal basis set. They are universal in the sense that they can be used with good accuracy in the whole series of hydrocarbon compounds. They are used throughout the calculations performed in this paper.

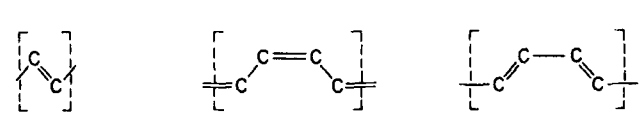
No information pertaining to the excited states is included in these universal atomic potentials. Although this could in principle be done,[10] it is not very useful in the framework of Hartree–Fock Hamiltonians, since Hartree–Fock excited states are known to have little meaning. As a result, considerable caution is necessary with regard to the VEH unoccupied levels. In fact, we frequently find σ^* bands abnormally low in energy.[12] However, for the planar conjugated systems we have considered, where σ-π separability occurs, we find that the computed bandgaps ($\pi \rightarrow \pi^*$) are in surprisingly good agreement with experiment.

In summary, the main advantages of the VEH model are: (i) it is completely theoretical; (ii) it is not basis set dependent; and (iii) it gives *ab initio* quality results with negligible computer time, due to the evaluation of only one-electron integrals and the complete avoiding of SCF iterative cycles.

III. RESULTS AND DISCUSSION

The VEH results for ionization potential (I.P.), bandwidth of the highest occupied band (BW), and π-electron band gap (E_g) are summarized in Table I. Also included in the table are experimental estimates of I.P. and E_g, where available, and the maximum conductivities (σ) obtained on doping with I_2 (a relatively weak electron acceptor) and AsF_5 (a strong electron acceptor). References are given in table for the experimental I.P., E_g, and σ values, as well as the source of the backbone geometry.[13–40] The theoretical I.P. values have been scaled downward by 1.9 eV to correct approximately for polarization energy and possible shortcomings of the model.[12] Experimentally determined polarization energies for a wide range of hydrocarbon materials have recently been reported as 1.7 ± 0.4 eV.[41] Though the 1.9 eV correction is quite reasonable, our I.P. results should be viewed as having been scaled to the experimental estimate for *trans*-polyacetylene.[13,14]

Three energetically nonequivalent backbone geometries can be envisioned for polyacetylene. The *trans* backbone is about 2–5 kcal/mole more stable per C_2H_2 unit than the *cis*-transoid which is ~ 0.2 kcal/mole more stable than the *trans*-cisoid.[42,43] VEH results for band structures, densities of states, and theoretical XPS spectra have been presented elsewhere,[12] along with a detailed comparison to the *ab initio* calculations Karpfen and Petkov performed for the *trans* case.[17]



trans cis-transoid trans-cisoid

TABLE I. Summary of VEH results for ionization potential (I.P.)[a], bandwidth of highest occupied band (BW), and band gap (E_g) of hydrocarbon polymers. All energies in eV; conductivities in S/cm.[b]

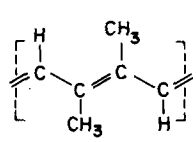
Polymer	I.P.	BW	E_g	$\sigma(AsF_5)$	$\sigma(I_2)$	Refs.[c]
Polyacetylene						
trans	4.7[4.7]	6.5	1.4[1.8]	1200	500	13–17
cis-transoid	4.8	6.4[d]	1.5[2.0]	...[e]	...[e]	15,18,19
trans-cisoid	4.7	6.5[d]	1.3	...	...	0
Polymethylacetylene	4.5	3.7	1.4	...	10^{-3}	20
Poly(1,6-heptadiyne)	4.4	2.5[d]	1.4[1.8]	0.1[f]	0.1[f]	21
Polydiacetylene						
acetylenic	5.1[5.2]	3.9	2.1[2.1]	0[e]	0	22–26
butatrienic	4.3	4.5		...	...	27
Poly(*p*-phenylene)						
coplanar	5.5	3.9	3.2	...	...	
twisted (22°)	5.6[5.5]	3.5[d]	... [3.4]	500	0	28–31
perpendicular	6.9	0.2[d]	...	...	...	
Poly(*m*-phenylene)						
coplanar	6.2	0.7[d]	4.5	...	...	
twisted (28°)	6.2	0.2	... [4.9]	0.001[f]	0	28,32,33
Poly(*p*-phenylene vinylene)	5.1	2.8	2.5[~3]	3	0	34,35
Poly(*p*-phenylene xylylidene)	5.6	2.5	3.4	...	...	36
Polybenzyl	6.5	0.6[d]	...	0	0	37,38
Polyyne	5.5	7.3	2.7	...	...	39
Polyacene						
regular	3.9	5.9	0	...	...	40
trans	4.1	5.6	0.3	...	...	
cis	3.9	5.8	0	...	...	

[a]Theoretical ionization potential after subtracting 1.9 eV to correct, approximately, for polarization energy of lattice. Experimental estimates for I.P. and E_g, where available, are given in brackets.
[b]Zero conductivity in the table indicates $\sigma < 10^{-5}$ S/cm; ellipses indicates unknown.
[c]References for experimental I.P., E_g, and σ values followed by reference for polymer geometry.
[d]The BW values for these cases refer to the smallest possible unit cell taking into account screw axis symmetry.
[e]When *cis* polyacetylene is doped, isomerization to *trans* takes place.[18]
[f]Polymer undergoes substantial chemical modification on doping.

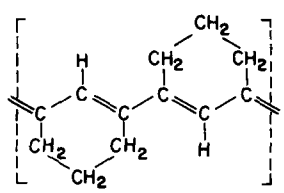
For the VEH calculations we have taken $R_{C=C} = 1.346$ Å and $R_{C-C} = 1.446$ Å for all three backbones[17] and the C–C–C angle equal to 125.3° for the *trans* backbone[17] and 127.3° for the *cis* backbones.[19] Little variation is evident in Table I for I.P., BW, and E_g for the three backbones. In fact, as we noted earlier,[12] the backbone variation is most evident in the σ electron characteristics—the differences being large enough to be detected with well-resolved XPS spectra.

For experimental band gaps, we have chosen the location of the lowest energy optical absorption peak for the sake of consistency among the different systems. Thus Table I lists 1.8 eV for *trans* polyacetylene,[15] rather than the widely reported 1.4 eV from the optical absorption threshold.[1] Nevertheless agreement is quite satisfactory, with comparison of theory and experiment suggesting a *cis*-transoid structure for the *cis*-polymer.

Several polyacetylene derivatives have been prepared, including polymethylacetylene[20] and poly(1,6-heptadiyne).[21]



polymethylacetylene

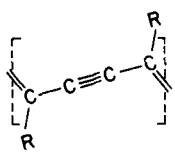


poly(1,6-heptadiyne)

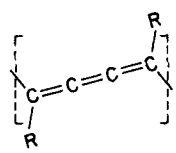
The VEH results for these two compounds, whose backbones have been assumed identical to that of *trans*-polyacetylene, show a slight downward shift in I.P., a substantial decrease in BW (due to the increased unit cell dimension corresponding to a symmetry lowering), and little change in E_g compared to polyacetylene. The conductivities achieved on doping with AsF_5 and I_2 are less than those for polyacetylene—a result which is consis-

tent with the trend in BW values. However, there are a number of other explanations for the lower σ values, including an increased tendency for substituted polyacetylenes to undergo chemical modification.[44] Note that two different structures can be envisioned for *trans* polymethylacetylene, depending on whether the methyl groups surround the double bonds or the single bonds. Both structures lead to similar theoretical values for I.P., BW, and E_g. Note that we have only considered the head-to-head conformer of polymethylacetylene, since the head-to-tail conformer would be grossly nonplanar due to steric interference between the methyl groups, all of which would be on one side of the chain.

Polydiacetylenes are usually produced via a solid-state reaction of single-crystal, substituted diacetylenes, RC≡C–C≡CR.[45] Under favorable packing conditions, which are dominated by the R groups, a single crystal polymer with highly one-dimensional electronic properties is obtained.[45] The polydiacetylene backbone can be visualized in the two forms shown below:



acetylenic



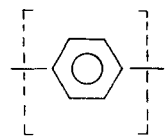
butatrienic

The acetylenic backbone is thought to be more stable by ~12 kcal/mol,[46] and most x-ray structures for polydiacetylene crystals yield this backbone.[26] Two structure determinations have yielded butatrienic-like bond lengths[47,48]; however, in both cases the backbones are strained.[49]

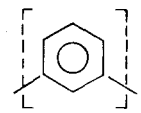
Our VEH calculations have considered only the case where R is hydrogen, since, from the polyacetylene results above, a relatively minor perturbation can be expected for substitution with $-CH_2R'$. For the acetylenic backbone, the geometry is taken from the x-ray structure for PTS,[26] the most studied polydiacetylene (R is $-CH_2SO_3C_6H_4CH_3$). The I.P. value is in excellent agreement with the photoionization threshold measurements on PTS due to Arnold.[22] The E_g value is also in good agreement with the experiment.[23] The I.P. and BW values suggest that polydiacetylene should behave in a similar manner to polyacetylene on doping. Doping of PTS with I_2 yields some conductivity increase[24,25] ($\sigma \sim 10^{-6}$ S/cm), while doping with AsF_5 yields gross chemical modification (due probably to chemical reactions with the substituent groups) the same is true of other polydiacetylenes tested.[24] Our results suggest that the electronic properties of polyterials and that R-group interference has led to the poor results obtained thus far. Unfortunately, the gas or liquid phase polymerization of unsubstituted diacetylene seems to yield an aromatized product, rather than the 1, 4-addition product obtained via solid-state polymerization.[50]

The VEH results for the "ideal" butatrienic backbone[27] suggest even more attractive properties. Formation of charged defects in polydiacetylene (analogous to soliton formation in polyacetylene) requires generation of butatrienic linkages. The fact that the acetylenic and butatrienic backbones are not energetically equivalent (unlike the two equivalent structures for *trans*-polyacetylene) suggests a higher degree of localization on ionization of the polydiacetylene chain. Note, however, that the same is true of all the structures we consider here with the possible exception of polyacene and poly(1, 6-heptadiyne). Even *trans*-polymethylacetylene has two energetically nonequivalent structures.

The structure of poly(*p*-phenylene) PPP is expected to be nonplanar with adjacent rings rotated by ~22° with respect to one another.[31] We have considered the three structures listed in Table I for illustration of the effect of this rotation on the electronic structure. The twisted structure yields results that



poly(p-phenylene)



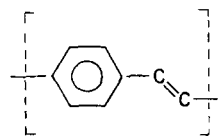
poly(m-phenylene)

are quite similar to the coplanar structure. However, a perpendicular orientation eliminates the potential for significant π-electron delocalization so that I.P. increases substantially and the BW decreases to 0.2 eV, a value comparable to that obtained for van der Waals bonded molecular crystals. An E_g value is given only for the coplanar structure, because of problems mentioned earlier regarding spurious σ^* bands.[12] The coplanar E_g value agrees well with experiment.[29]

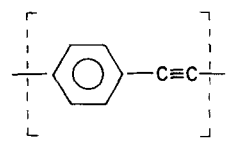
PPP yields σ values comparable to polyacetylene with AsF_5 doping but does not yield high conductivities with I_2.[2,29] The VEH results are consistent with this observation in that the I.P. for PPP is 0.9 eV higher than for polyacetylene.

Poly(*m*-phenylene) PMP is predicted to have a substantially larger I.P. and a substantially smaller BW than PPP. Therefore, we expect, based on the VEH results, that PMP would be an unlikely candidate for a conducting polymer. In fact the conductivity obtained on AsF_5 doping is fairly small (10^{-3} S/cm). In addition, present experimental results strongly suggest that PMP cross-links on exposure to AsF_5 to form a more extended aromatic network.[28,32]

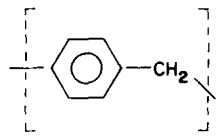
The next three entries in Table I involve derivatives (copolymers) of PPP:



poly(p-phenylene vinylene)



poly(p-phenylene xylylidene)



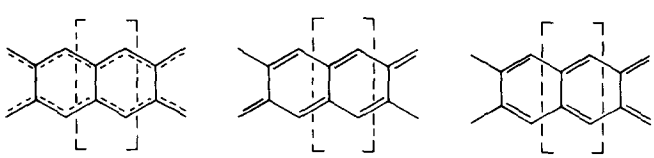
polybenzyl

Poly(*p*-phenylene vinylene) can be considered as a regular copolymer of PPP and *trans*-polyacetylene. It is only available as oligomers ($n \sim 8$).[34] The VEH calculations for a coplanar conformation yield I.P. and E_g values intermediate between polyacetylene and PPP, with a BW less than either of the parent polymers. AsF_5 doping yields $\sigma \sim 3$ S/cm while I_2 doping has been unsuccessful[34]; the latter may result from the increased I.P. or the low molecular weights of available samples. The VEH results for coplanar poly(*p*-phenylene xylylidene) are very similar to PPP, except for the decreased BW. This polymer has not yet been investigated but should show behavior similar to PPP.

The large value of IP and the low value of BW in polybenzyl are due to the combined effects of the presence of saturated carbons in the backbone and the almost perpendicular arrangement of two consecutive phenyl rings in the structure.[38] Conductivities are less than 10^{-6} S/cm for AsF_5 and I_2 doping.

The remaining materials, polyacene and polyyne ("linear carbon") have been reported as high molecular weight polymers,[51] but these reports have not been unambiguously verified. The geometry for polyyne, $\leftarrow C{\equiv}C \rightarrow$, is taken from Karpfen's double zeta quality geometry optimization which indicates a larger bond-length alternation (0.16 Å) than in polyacetylene (0.10 Å).[39] The VEH results suggest that polyyne, though intrinsically interesting because of its novel structure, is not of special interest in relation to its predicted electronic properties in the undoped state. The equal bond length structure for polyyne, which is substantially higher in energy at the Hartree–Fock level,[39] yields zero band gap and I.P. = 4.2 eV.

Three different structures have been investigated for polyacene, which can be viewed as consisting of two regularly crosslinked polyacetylene chains. The bond length for the C–C bonds connecting the two chains is taken as 1.44 Å in all three structures. For the regular structure, equal bond lengths



(1.40 Å) are assumed for the two chains, in agreement with the trends observed in the middle of tetracene and pentacene.[40] Otherwise, we take $R_{C=C}$: 1.36 Å and R_{C-C} : 1.42 Å,[40] in the sequence indicated in the structural drawings for *trans* and *cis* polyacene. All intrachain bond angles are taken as 120°. Low I.P. values and large BW values are predicted for each structure. E_g values are either quite low or identically zero, as expected based on extrapolation of polyacene oligomer data.[52]

IV. SUMMARY

We conclude that the valence effective Hamiltonian technique offers a reliable, yet inexpensive, method for calculating the valence band electronic properties of polymers. Ionization potentials, after a 1.9 eV adjustment for polarization effects, are in excellent agreement with the available experimental results and correlate quite well with the conductivity results for weak versus strong electron acceptors. The width of the highest occupied band in the series of polymers considered shows a satisfying qualitative correlation to the conductivities achieved on doping. Furthermore, the band gaps for the planar systems are in good agreement with experiment. Taken together these results suggest that the VEH technique offers a rather complete picture of the electronic properties of hydrocarbon polymers. We are now in the process of extending the computations to sulfur containing polymers.

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