

Brief Reports

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Electron-correlation effects in the photoelectron spectrum of polyacetylene

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Electron-correlation effects in the photoelectron spectrum of polyacetylene are analyzed. Hole mixing and breakdown of the one-particle picture are obtained and interpreted by means of *ab initio* Green's-function calculations based on canonical crystal orbitals. The results represent explicit theoretical evidence that electron correlation effects are essential for an understanding of the photoelectron spectrum of polyacetylene at binding energies larger than 17 eV with respect to the Fermi level.

I. INTRODUCTION

Electron-correlation effects are known to play a significant role in the understanding of photoelectron spectra of finite molecules.¹ For polymers, in particular polyacetylene, *ab initio* calculations of correlation effects on the band edges of the outer-valence bands have been performed by the Rayleigh-Schrödinger perturbation theory² and Green's-function methods.³ Recently, correlation effects in the complete valence region of the photoelectron spectra of polyacetylene and polyethylene have been investigated by an *ab initio* Green's-function method.⁴

The present calculations extend the work described in Ref. 4 by also taking hole-mixing effects into account which were previously not included. Hole mixing may become important when two bands of the same symmetry come close to each other. This is particularly the case for the σ bands of polyacetylene at the end points of the Brillouin zone.

II. COMPUTATIONAL

Ab initio crystal-orbital^{5,6} calculations were performed to determine the Hartree-Fock band structure and eigenvectors. Double-zeta basis sets⁷ and the Suhai geometry⁸ have been employed. (This geometry has been chosen among other possibilities¹⁶ because it was also determined at the level of the second-order Møller-Plesset perturbation theory.) Nine neighboring cells have been taken into account for the electron-electron interaction and 801 k points in the Brillouin-zone integrations in the Hartree-Fock calculations, two neighboring cells and nine k points in the perturbation calculations. Spline interpolation has then been used to obtain the correlation shifts for 801 k points.

Convergence of the ionization potentials with the number of interacting neighbor cells N_G and number of k

points N_K is demonstrated in Fig. 1. The corresponding quasiparticle shifts have been calculated with and added to the Hartree-Fock results for $N_G=9$ and $N_K=801$. Due to the localization of the Wannier functions, convergence of the correlated results obtained in this way is faster with respect to N_G and N_K than that of the Hartree-Fock results. Furthermore, the trends of correction are parallel for all bands considered here, so that the spectral density on a relative energy scale (referred to the Fermi level) is expected to be satisfactory with the above choices of N_G and N_K . This is in agreement with the results of König and Stollhoff¹⁷ who find on-site correlation effects to be most important in polyacetylene.

The quasiparticle bands are calculated as solutions of the inverse Dyson equation which differs from its molecular form⁹ in the polymer case¹⁰ only in that the indices of the Green's-function matrix in the latter case consist of

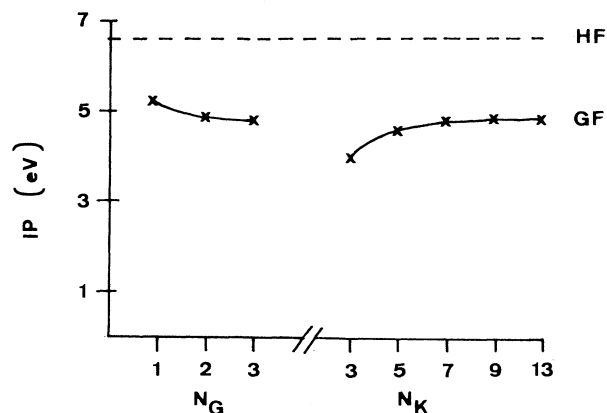


FIG. 1. Dependence of the ionization potential (IP) of *trans*-polyacetylene on the number of interaction neighbor cells N_G and the number of k points N_K . HF denotes the converged Hartree-Fock value, GF the Green's-function results.

band quasimomentum indices. The Dyson equation has been solved with a second-order irreducible self-energy part $M(\omega)$,

$$M_{PQ}^{(2)}(\omega) = \sum_{JKL} V_{PJKL} (2V_{KLQJ} - V_{KLJQ}) \\ \times \delta_{k_p, k_q} \delta_{k_j, k_k + k_l - k_p} \\ \times [n_J \bar{n}_K \bar{n}_L (\omega + \epsilon_J - \epsilon_K - \epsilon_L + i\eta)^{-1} \\ + \bar{n}_J n_K n_L (\omega + \epsilon_J - \epsilon_K - \epsilon_L - i\eta)^{-1}],$$

where $V_{PJKL} = \langle P(1)J(2)/K(1)L(2) \rangle$ are the two-particle integrals over crystal orbitals, n_J are the occupation numbers ($n_J = 1$ for a doubly occupied band, $n_J = 0$ for an empty band), $\bar{n}_J = 1 - n_J$, and η is a positive infinitesimal, tending to zero in the distributional sense.

Since the Green's-function matrix is diagonal in the k index, it remains for each k point to diagonalize a matrix over the band indices. The nondiagonalities encountered here are referred to as hole-mixing effects¹ and have previously been neglected in polymer calculations.⁴

The spectral density of the advanced part of the one-particle Green's function A^- is evaluated as a quasicontinuous sum over the occupied bands,⁴

$$A^-(\omega) = \sum_{I,\mu}^{\text{occ}} P_{I\mu} \delta(\omega - \omega_{I\mu}),$$

where $I = (n_i, k_i)$, μ numerates the satellite bands, and $P_{I\mu}$ are the pole strengths, i.e., the residues of eigenvalues of the Green's-function matrix.

III. RESULTS AND DISCUSSION

The resulting poles of the one-particle Green's function for selected k points are given in Table I. The residues of the diagonal elements of the Green's-function matrix at the $(I\mu)$ th pole, $a_{JJ\mu}$, are also given; they are related to the pole strengths by $a_{JJ\mu} = P_{I\mu} |c_{J\mu}|^2$, where $c_{J\mu}$ is the J th component of the corresponding eigenvector. Nondiagonalities are mainly observed for the 3σ and 4σ inner-valence bands near the end point of the Brillouin zone. Furthermore, the 3σ band undergoes a splitting into several satellite bands, i.e., a breakdown of the one-particle picture, and the 4σ band has a satellite band near the end point of the Brillouin zone. The complete corre-

TABLE I. Poles of the one-particle Green's function. (Residues in parentheses. Energies relative to the Fermi edge, in eV.)

Band	$k=0$	$k=\pi/2a$	$k=\pi/a$
1π	-7.28(0.48)	-4.64(0.46)	0.00(0.46)
6σ	-6.66(0.46)	-7.16(0.48)	-9.50(0.06/0.41) ^a
5σ	-8.00(0.49)	-10.73(0.48)	-10.55(0.42/0.07) ^a
4σ	-10.95(0.44)	-12.35(0.45)	-17.25(0.08) -18.01(0.46)
3σ	-21.75(0.09) -21.82(0.25) -22.60(0.07)	-20.52(0.08) -20.69(0.19) -20.87(0.13)	-18.27(0.23) -18.45(0.16) -19.50(0.06)

^aThe residues for these bands belong to the $5\sigma/6\sigma$ indices in the given order.

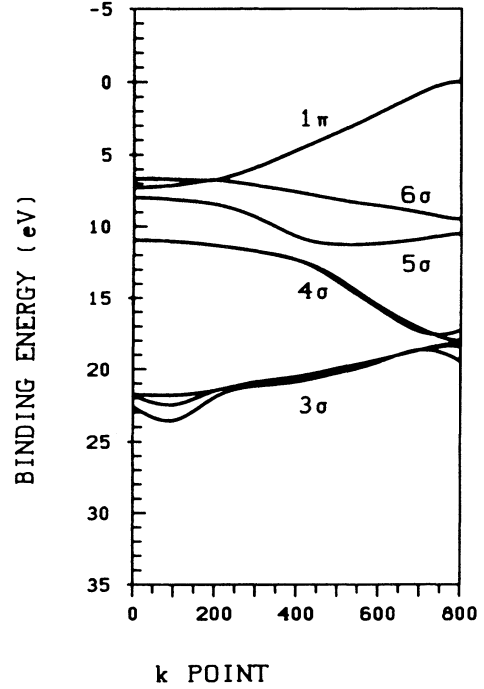


FIG. 2. Correlated energy-band structure of *trans*-polyacetylene. Binding energies (in eV) are relative to the Fermi edge.

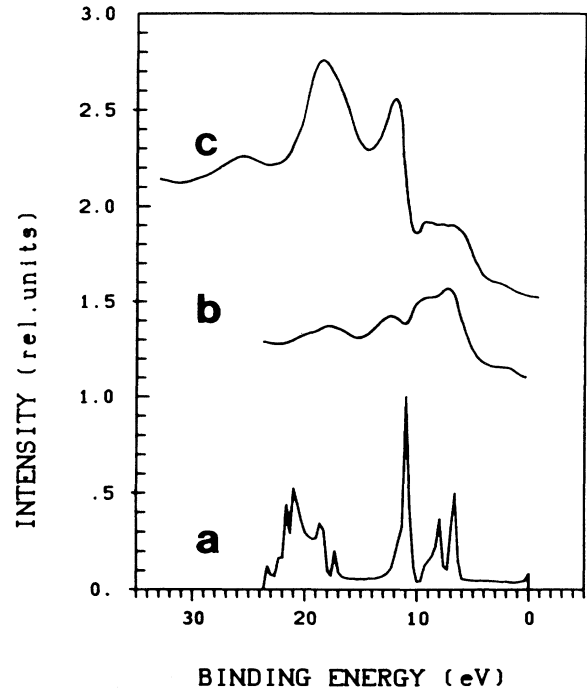


FIG. 3. Spectral density of the one-particle Green's function. (a) Theoretical density, (b) experimental photoelectron spectrum from Ref. 11, and (c) XPS spectrum from Ref. 15. Binding energies (in eV) are relative to the Fermi edge.

lated valence-band structure of polyacetylene is given in Fig. 2, the corresponding spectral density in Fig. 3.

The spectral density can be used to interpret the photoelectron spectrum of polyacetylene. The experimental synchrotron radiation excited spectrum of Rasmusson *et al.*¹¹ ($h\nu=125$ eV) and the x-ray photoemission spectroscopy (XPS) spectrum of Keane *et al.*¹⁵ are included for comparison in Fig. 3. All binding energies in the figures and in the table are referred to the Fermi level (top of the highest valence band) to align with the experimental spectrum. The main features of the experimental spectrum at about 7, 9, and 12 eV are reproduced by the calculations, and the interpretation of these features is in agreement with other recent calculations, see Refs. 11–14, and references therein. The explanation of the extended feature between 17 and 29 eV in the experiment is less satisfactory, but more interesting. The corresponding part of the theoretical spectrum is substantially influenced by breakdown effects. This is due to an interaction of the 3σ ionized states with shake-up states accompanying 4σ , 5σ , and 6σ ionization. In fact, one has to assume that higher orders of the electron-electron interaction (than the second order considered here) are responsible for the extended satellite structures observed in the XPS spectrum of polyacetylene.¹⁵ However, the redistribution of intensity in the 3σ region compared to the Hartree-Fock results indicates the correct trend to explain the experimental findings by breakdown effects in the inner-valence region.

IV. CONCLUSIONS

We have found explicit theoretical evidence that electron-correlation effects, in particular, the breakdown of the quasiparticle picture in the inner-valence region, are essential for an understanding of the photoelectron spectrum of polyacetylene at binding energies larger than 17 eV. The present results indicate that the structures in the higher-energy region represent 3σ one-hole states strongly interacting with outer-valence-based shake-up states.

While the experimental XPS structure shows a complete splitting of the 3σ band, our calculation can only reproduce the trend of the formation of the satellite band. The remaining discrepancy must be attributed to the use of a second-order self-energy part which is known to yield only semiquantitative results. However, the calculations permit an assignment of the experimental structures in all parts of the spectrum which was made possible by explicit inclusion of correlation effects at the *ab initio* level.

While the physics involved in outer-valence ionization of solids is essentially that of the electronic-polaron model,^{18–20} leading to shifted quasiparticle bands, we have a different mechanism in the inner-valence region. This breakdown of the quasiparticle picture is known from finite molecules¹ and has become tractable for polymers recently.⁴ The present calculations are in keeping with this by showing that hole mixing does not have much influence on the results in the case of polyacetylene.

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