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Ab initio Green's-function calculations on the Auger spectra of polyethylene

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An *ab initio* Green's-function method for calculating the Auger spectra of polymers is presented. The method makes use of the translational symmetry of the polymer by transforming the two-particle Green's function to an excitonlike representation. Electron correlation effects are included by a renormalization procedure employing quasiparticle bands obtained from a one-particle Green's-function calculation. Comparison of the calculated with the experimental spectrum shows a rapid convergence with the size of the elementary cell and supports earlier interpretations that some shake-off satellite structure must contribute to the spectrum.

I. INTRODUCTION

The theory of the Auger spectra of polymers has, until now, been mostly based on solid-state methods. They involve the self-convolution of the density of states[1] as well as distorted line shapes described by the Cini-Sawatzky expression.[2,3] The most intensively studied polymer Auger spectrum is that of polyethylene. For that system several experimental spectra have been published,[4–6] which differ in some details due to the different procedures in calibration of charging effects and different deconvolution procedures.

On the theoretical side, apart from the above-mentioned approaches, the effects of final-state localization have been studied[7] and the importance of satellite structures has been postulated.[8] To assess the quality of those essentially semiempirical approaches and to reexamine their conclusions it would be desirable to have also *ab initio* calculations available for comparison. On the *ab initio* level there have been Green's function calculations on the Auger spectra of clusters modeling short oligomer sequences of polyethylene.[9] Those calculations have demonstrated the relatively fast convergence of the cluster spectra to the bulk spectrum. However, due to the cluster size a renormalization of one-particle lines to account for more correlation effects was not attempted at that time.

The approach presented here makes explicit use of the translational symmetry of the polymer and starts from *ab initio* crystal-orbital band-structure calculations. The transformation of the two-particle Green's function to an excitonlike representation yields cell-block equations which converge much faster than the cluster calculations to the bulk limit, and thus permit a more accurate treatment of correlation effects at the *ab initio* level.

II. METHOD

The kinetic energy of the Auger electrons is $E_{\text{kin}}=I_c'-I_v''$ where I_c' is the core ionization potential and I_v'' is the double ionization potential (DIP) for the corresponding final state. The DIP's and the corresponding transition rates determine, therefore, the Auger line shape on a binding-energy scale. In *ab initio* Green's function calculations on molecular Auger spectra[9–15] one makes use of the fact that the two-particle Green's function has poles at the $-$DIP values. In the case of an infinite periodic system it is convenient to transform the two-particle Green's function from the Bloch representation (two crystal orbital indices) to a mixed representation characterized by a separation cell index and a quasimomentum index K for localized two-hole states, similar to the exciton representation for particle-hole states.[16] In that representation, the Bethe-Salpeter equation is given by

$$\underline{G}^{-1}(K,\omega)=\underline{G}^{(0)-1}(K,\omega)-\underline{K}(K)\ , \tag{1}$$

where $\underline{G}$ is the ω-dependent Green's-function matrix and $\underline{G}^{(0)}$ and $\underline{K}$ are the matrices of the interaction-free two-particle Green's function and first-order irreducible vertex part, respectively,

$$\underline{G}^{(0)}_{s'i'j'sij}(K,\omega)=\gamma_{ij}\delta_{i'i}\delta_{j'j}(2\pi)^{-1}\int_{-\pi}^{\pi}dk\,\exp[ik(R_{s'}-R_s)]\sum_{\mu,\nu}P_{i\mu}(k)P_{j\nu}(K-k)/[\omega-\omega_{i\mu}(k)-\omega_{j\nu}(K-k)] \tag{2}$$

and

$$\mathcal{K}_{s'i'j'sij}(K)=\sum_{u}\exp(-iKR_u)\left(\left\langle {u \atop i'}{+s'u \atop j'}\middle|{s0 \atop ij}\right\rangle-\left\langle {u \atop i'}{+s'u \atop j'}\middle|{0s \atop ji}\right\rangle\right)\ . \tag{3}$$

The following notation has been used: s and s' are cell indices, i',i,j,j' are band indices, $\gamma_{ij}=-1$ if both bands i,j are occupied, $\gamma_{ij}=+1$ if both are unoccupied in the Hartree-Fock ground state; $\omega_{i\mu}(k)$ are the renormalized one-particle bands where i is the band index, k the quasimomentum, and μ runs over the possible shake-up satellite bands including the quasiparticle band if existing; $P_{i\mu}(k)$ are the corresponding pole strengths (residues of the one-particle Green's function in diagonal approximation[17]). The two-electron integrals are defined as

$$\left\langle {}^{s'u}_{i'j'} \middle| {}^{s0}_{ij} \right\rangle = \int w_{i'}^{s'}(1)^{*} w_{j'}^{u}(2)^{*} r_{12}^{-1} w_{i}^{s}(1) w_{j}^{0}(2)\, d\tau_1 d\tau_2 \ , \tag{4}$$

where w_i^s is a Wannier function belonging to band i and centered in cell s. The Wannier functions are localized by phase factor optimization.[18] The renormalized one-particle band structure has been taken from a recent one-particle Green's function calculation on the complete valence region of polyethylene,[19] using also the same one-particle wave functions as in that calculation.

The poles $\omega_\nu = -I''_\nu$ are obtained as the zeros of the eigenvalues of the inverse Green's function matrix given in Eq. (1). In a first-neighbors' interaction approximation one can partition the matrix $\underline{G}^{-1}$ into blocks belonging to cell indices $s = -1, 0, 1$:

$$\underline{G}^{-1} = \begin{bmatrix} \underline{A}_{-1} & \underline{B}_{-1} & \underline{0} \\ \underline{B}^{+}_{-1} & \underline{A}_{0} & \underline{B}_{1} \\ \underline{0} & \underline{B}^{+}_{1} & \underline{A}_{1} \end{bmatrix} . \tag{5}$$

Using Löwdin's subspace-partitioning technique,[20] one can reduce the problem of finding the zero eigenvalues of Eq. (5) to that of finding the zero eigenvalues of the following effective one-cell matrix:

$$\tilde{\underline{A}} = \underline{A}_0 - \underline{B}^{+}_{-1}(\underline{A}_{-1})^{-1}\underline{B}_{-1} - \underline{B}_{1}(\underline{A}_{1})^{-1}\underline{B}^{+}_{1} \ . \tag{6}$$

Improvement on the first neighbors' interaction approximation is possible by extension of Eq. (5) to more cell indices or by enlarging the elementary cell; the second possibility has been chosen in the present study.

The transition rates are obtained in a one-center model[21] as

$$R_\nu(K)dK \sim d^{(S,T)} \sum_{l,m,i,j,i',j'} M^{*}_{ijlm} M_{i'j'lm} \mathrm{Res}[-\underline{G}_{0ij0i'j'}(\omega_\nu, K)]dK \ , \tag{7}$$

where M_{ijlm} is the matrix element of the electronic Hamiltonian between Hartree-Fock states where the initial state has a core hole on a carbon atom in the reference cell (index $s=0$) and the final state has holes in bands i and j and one electron in a spherical continuum orbital ϕ_{lm} centered at the core hole site; the residue of $-\mathcal{G}$ is taken at the pole corresponding to the transition energy. The matrix elements M_{ijlm} are evaluated in the one-center approximation,[21] employing the radial integrals of McGuire.[22]

A grid of 501 k points has been used in the Brillouin-zone integrations via the summed Simpson rule and the line spectra obtained in that way have been convoluted with Gaussians of appropriate uniform width for each spectrum to account for vibrational broadening and experimental resolution. From the treatment of finite molecules it is known that the *ss* components are broadened much more by vibrations than the *pp* components. In the absence of *ab initio* values for those widths in the present case it was, however, not attempted to further improve the calculated spectra by adjusting the *ss*, *sp*, and *pp* widths separately.

III. RESULTS AND DISCUSSION

The calculations on polyethylene have been performed employing as elementary cell a $(CH_2)_N$ unit with $N = 1, \ldots, 3$. The resulting theoretical line shapes are given in Fig. 1 and compared with the experimental spectrum of Kelber *et al.*[5,7] It should be mentioned, however, that another choice[8] of the energy scale in accordance with the Dayan-Pepper spectrum[6] could lead to a difference in the binding energies of about 5 eV. The difference is due to uncertainties in the charging of the ple which has been determined to shift energies by 4.0 eV + 0.6 eV in the case of x-ray excitation,[5] whereas Dayan and Pepper used electron excitation and observed an opposite charging effect (of at most 5 eV) which they tried to minimize by increasing the beam raster velocity.

Convergence of the theoretical line shape with the size of the elementary cell is relatively fast. There are two reasons for this behavior. First, the mixed representation in Eqs. (2) and (3) allows the two holes to move together through the polymer with a given quasimomentum K. Second, the two holes are effectively separated from each other by no more than a few methylene units, as can be seen from the non-negligible hole-hole repulsion (which amounts to 7.52 eV for the double-ionization threshold for singlet states).

Comparison of the theoretical results with the experimental spectrum shows that agreement is best in the midenergy part (about 35–45 eV), while the intensity is somewhat underestimated by the calculation in the high- and low-energy parts. A similar disagreement between a semiempirically obtained *KVV* line shape and the experimental spectrum has been observed by Hutson and Ramaker[8] and has been assigned to resonantly excited autoionization satellites on the high kinetic energy side (with a spectator or participant electron in an excitonic level) and initial-state and shake-off satellites on the low kinetic energy side.

Since the present calculations incorporate correlation effects (and thus account for two-hole localization, which does contribute to the structures[7]) the above assignments of line-shape differences between theory and experiment to satellite transitions seem to be also valid at the level of *ab initio* calculations.

As is known[23,24] the density of states of polyethylene can be divided into two parts, one belonging to a band of

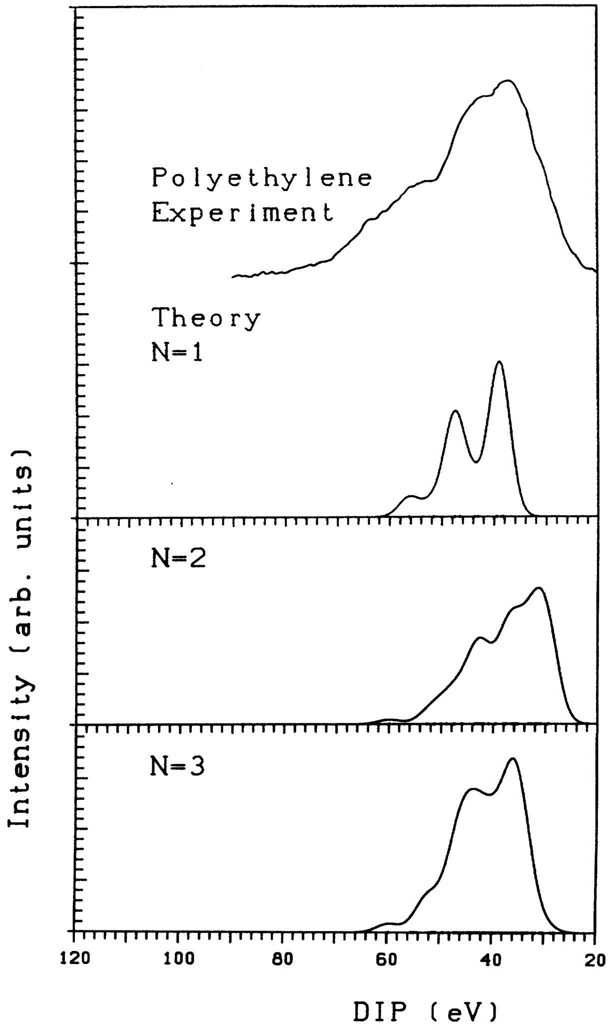

FIG. 1. Calculated *KVV* Auger line shapes of polyethylene for different extensions of the elementary cell $(CH_2)_N$, $N = 1, \ldots, 3$. Comparison is made with the experimental spectrum of Kelber *et al.* (Refs. 5 and 7). Binding energy scale in eV, intensities in relative units.

mainly *s*-type character and one being due to two bands of mainly *p*-type character. Referring to those two sets of states as inner- and outer-valence states, one can identify those portions in the *KVV* Auger spectrum which derive intensity from components of the eigenvectors of the Green's matrix belonging to hole pairs in outer-outer, outer-inner, or inner-inner type states. This is done in Fig. 2. The three portions are overlapping, but the outer-outer components seem to be responsible for the main part of the intensity of the first maximum at low binding energy. The inner-inner components have more structure and are responsible for the intensity at high binding energies, while the outer-inner components seem to contribute less distinctly to the structures.

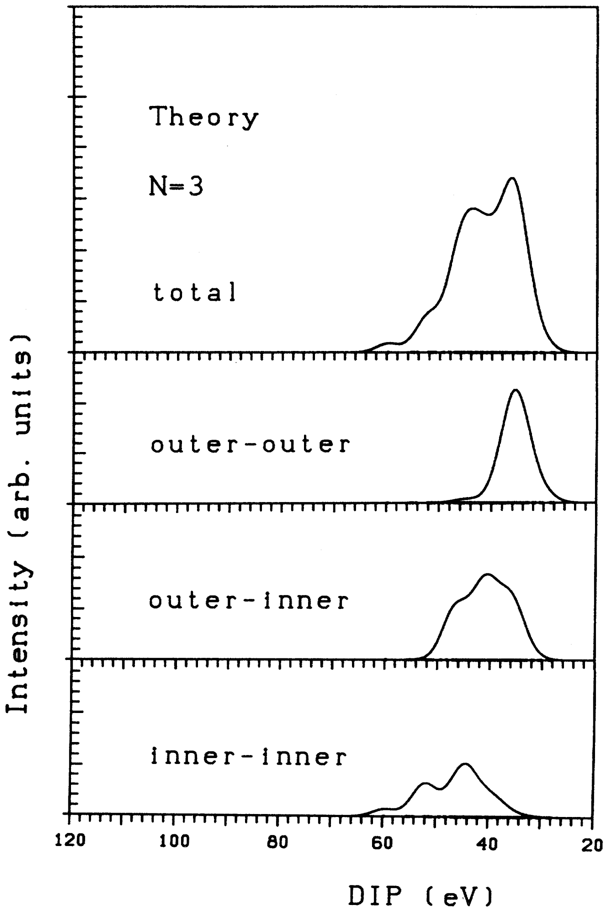

FIG. 2. Decomposition of the theoretical *KVV* Auger line shape into contributions coming from different valence double-hole components (outer-outer, outer-inner, inner-inner). Binding energy scale in eV, intensities in relative units.

IV. CONCLUSIONS

The above calculations on polyethylene have shown that *ab initio* Green's function calculations on the Auger spectra of polymers are an appropriate tool to account for correlation effects in periodic covalent systems. It was, therefore, possible to support earlier proposals which identified some satellite contributions to the experimental Auger spectra of polyethylene, and to assign the main structures of the *KVV* part to transitions with specified valence double-hole components.

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