Correlated Prediction of the Photoelectron Spectrum of Polyethylene: Explanation of XPS and UPS Measurements

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The correlated quasiparticle energies for valence bands of polyethylene have been calculated, *ab initio*, employing many-body perturbation theory. Electron correlation effects for the bands vary from 1.5 to 5.4 eV. The MBPT(2) band energies accurately explain the measured photoelectron spectra (XPS, UPS) of polyethylene and resolve long-standing disagreements among these experiments. Density functional theory fails to provide agreement with experiment. This example demonstrates the critical role of correlated *ab initio* theory in obtaining accurate band structures for extended systems. [S0031-9007(96)01419-6]

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X-ray (XPS) [1–4] and ultraviolet photoelectron spectroscopy (UPS) [5–8] provide rich information about the valence bands of extended systems. The further development of angle-resolved UPS (ARUPS) can even be used to directly observe the band structures. In the last two decades, these two methods have been frequently used to elucidate the valence electron structures of synthetic organic polymers. Among them, polyethylene is well studied [2–4,6–8].

Various semiempirical methods [8] and Hartree-Fock (HF) calculations [9–11] have been used to attempt to interpret polyethylene's measured UPS and XPS spectra. A few semiempirical methods, among many, provided some agreement with experiment in selected energy ranges, but failed in others [8]. HF offered a better description of the general features [9–11], but, in the absence of electron correlation, which is crucial in a first principle description for both finite molecules and extended systems [12–15], the HF band structure would require a 2 eV shift and an 80% contraction in scale to compare with experiment [7]. However, there are discrepancies in the experiments that require resolution. The experimental XPS data [3] finds a peak at 12.6 eV that is not seen in either the other XPS work [4] or ARUPS experiments [8] and misses a peak at 15.4 eV, seen in the other experiments [4,8]. The ARUPS result misses the 9.6 eV XPS peak [8]. Predictive correlated theory can help to resolve these questions.

Many-body perturbation theory (MBPT) and its infinite-order coupled cluster (CC) generalizations provide a systematic way to obtain the essential effects of electron correlation in finite systems [14,15]. A few efforts have been made to formulate and apply such tools for extended systems, usually focusing on band gaps [16,17]. The MBPT(2) band gaps are larger than the experimental results primarily because of the unphysical HF conduction bands, although MBPT(2) provides great improvement compared to HF band gaps [17]. Photoelectron spectra, however, depend upon the valence bands, making MBPT(2) an even better approximation.

In this Letter, we report the initial MBPT(2) quasiparticle valence band energies for polyethylene. We will show that unlike DFT, the *ab initio* MBPT(2) description in a polarized 6-31G** basis [18], properly converged with lattice summations and integration over reciprocal space [17], accurately explains the XPS and UPS spectra. We will also show that the disagreements among the experiments can be resolved by considering the width of the x-ray and UV radiation.

Polyethylene is considered in its all-*trans* conformation which has a screw axis S_2 along the chain direction. The unit cell is CH_2. Unlike polyacetylene, there are only slight differences among the geometries determined either by experiment or by theory. In our calculation, we will use the x-ray structure: $r_{CC} = 2.89$ bohr, $r_{CH} = 2.02$ bohr, $\angle HCH = 107.0$ deg, and $\angle CCC = 112$ deg [10,19].

The quasiparticle band energies are defined as the electron ionization potentials for valence bands beyond the HF approximation, of which the MBPT(2) expression is

$$\epsilon_P^{[\mathrm{MBPT(2)}]} = \epsilon_P^{\mathrm{HF}} + \sum_I \sum_{AB} \frac{2|\langle PI||AB\rangle|^2 - \mathrm{Re}[\langle PI|AB\rangle\langle BA|PI\rangle]}{\epsilon_P^{\mathrm{HF}} + \epsilon_I^{\mathrm{HF}} - \epsilon_A^{\mathrm{HF}} - \epsilon_B^{\mathrm{HF}}} + \sum_{IJ} \sum_{A} \frac{2|\langle PA||IJ\rangle|^2 - \mathrm{Re}[\langle PA|IJ\rangle\langle JI|PA\rangle]}{\epsilon_P^{\mathrm{HF}} + \epsilon_A^{\mathrm{HF}} - \epsilon_I^{\mathrm{HF}} - \epsilon_J^{\mathrm{HF}}}, \quad (1)$$

where ϵ_P^{HF} is the HF band energy, P, I, J, and A, B denote the occupied and unoccupied Bloch orbitals, respectively. More explicit formulas are presented elsewhere [17,20].

Our MBPT(2) program for extended systems for the total energy and band structure is combined with HF solutions from PLH93 [17,21]. In our calculations, we employ 34 unit cells (CH_2) in the lattice summations and 41 points in the first Brillouin zone for integration over the reciprocal space to ensure that the numerical results are converged. This is critical for MBPT(2) calculations in extended systems [17].

Figure 1 shows the HF, two density functional theory (DFT) variants (LDA and gradient corrected BLYP) [22],

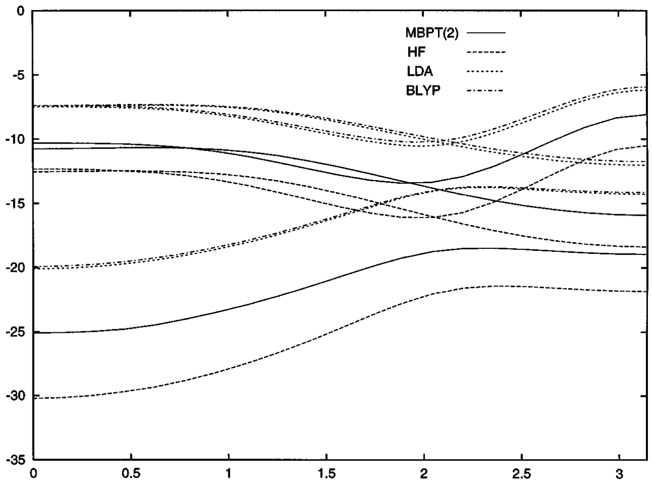

FIG. 1. The HF, LDA, BLYP, and MBPT(2) valence bands of all-*trans* polyethylene with basis set 6-31G as a function of k.

and MBPT(2) band structures of polyethylene calculated with the 6-31G basis set. The MBPT(2) bands are above the HF and below the DFT ones. The correlation shift is different at different points in the bands [23], being around 2 eV for the first two bands. For the third band, the shift is about 5 eV at 0 and 3 eV at π/a.

Figure 2(a) shows the density of states (DOS) for the MBPT(2) bands shown in Fig. 1. The peaks in the DOS have corresponding maxima in the photoelectron spectra and can be well determined experimentally. The calculated values for these peaks using HF and MBPT(2) with 6-31G and 6-31G** bases, the latter containing d functions on C and p functions on H, are compared to experiment in Table I. As polarization functions are essential to measuring correlation effects, we see shifts of 0.1 to 0.3 eV.

The XPS and UPS for polyethylene are measured in the solid phase. However, it is known that the weak van der Waals intermolecular interaction causes only about a 0.1 eV energy-band dispersion [24], which is negligible compared with the large intramolecular dispersion of 5 eV. The difference between the binding energy of an individual chain in the gas phase and that in the solid phase is the work function, a constant determined to be in the range of 4.5 to 4.8 eV. The experimental values listed in Table I take the work function as 4.8 eV [8].

The line intensities of the measured spectra depend on both the photoionization cross sections and the frequency distribution of the incident radiation. The photoionization cross sections are functions of the angle of incident radiation, the energy of the radiation, and the angle of the emitted electrons. Hence, the ARUPS spectra varies with these three parameters [8]. Here we focus only on the peaks of the DOS when we compare with the ARUPS spectra. For the XPS spectra, we simply use the Gelius model [25] for the relative photoionization cross section taking the photoionization cross section of the C_{2s} bonding band to be 13 times larger than that for the other two valence bands.

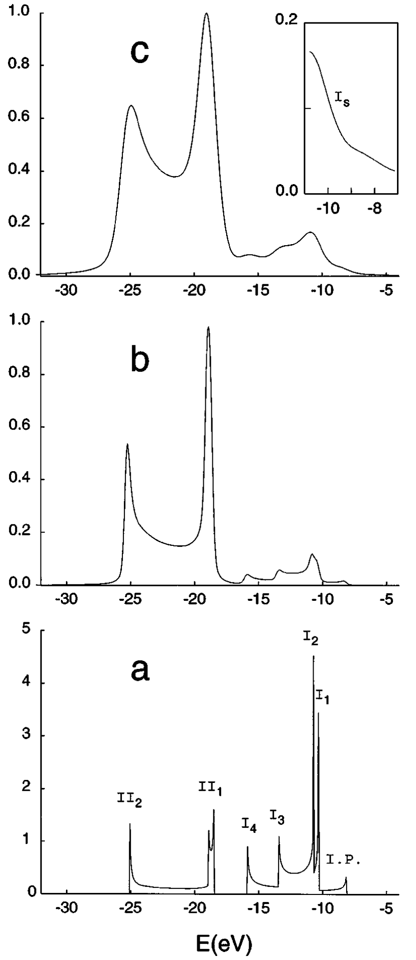

FIG. 2. The MBPT(2) photoelectron spectra for all-*trans* polyethylene with basis set 6-31G. (a) Density of states, (b) photoelectron spectrum with $\Gamma = 0.2$ eV, and (c) photoelectron spectrum with $\Gamma = 0.75$ eV.

The energy distribution of the incident radiation can be described by a linear combination of Lorentzian and Gaussian curves with a half width at half maximum Γ. Then the relative line intensities are expressed as

$$I(E) = \sum_i t_i d_i(E') \left\{ \frac{w_l}{\pi} \frac{\Gamma}{(E - E')^2 + \Gamma^2} + \frac{w_g}{\Gamma} \sqrt{\frac{\ln 2}{\pi}} \times \exp\left[-\frac{\ln 2}{\Gamma^2} (E - E')^2 \right] \right\} dE', \quad (2)$$

where t_i is the ith band's photoelectron cross section, $d_i(E')$ is the band's DOS, while w_l and w_g are the weight of the Lorentzian and Gaussian curves, respectively.

With $\Gamma = 0.2$ eV and using equal weight for the two curves, we obtain the MBPT(2) photoelectron spectrum described in Fig. 2(b). Because of the strong overlap, I_1 and I_2 merge into one peak as do the two peaks of II_1. Other peaks in the DOS have their own corresponding maxima in Fig. 2(b). The first ionization potential (IP) has a small but visible peak.

TABLE I. Comparison among the peaks in the density of states calculated using HF, BLYP, and MBPT(2) with basis sets 6-31G and 6-31G**, respectively, and those measured by XPS and ARUPS.

		IP	I_s[a]	I_1	I_2	I_x	I_3	I_4	II_1	II_2
HF	6-31G	10.51		12.31	12.52		16.08	18.37	21.43	30.21
HF	6-31G**	10.55		12.37	12.64		15.99	18.27	21.50	30.03
BLYP	6-31G	5.93		7.39	7.40		10.24	11.73	13.70	19.92
MBPT(2)	6-31G	8.08	9.50	10.32	10.75		13.44	15.91	18.48	25.09
MBPT(2)	6-31G**	8.40		10.59	11.06		13.54	15.99	18.39	24.66
XPS [3]	Polyethylene	8.6	9.6	11.2		12.6	13.8		18.0	23.6
XPS [4]	$C_{36}H_{74}$		9.8	11.1			13.7	15.4	18.0	23.8
ARUPS [8]	$C_{36}H_{74}$			10.5–12.0[b]			14.0	15.5	18.3	24.6

[a] MBPT(2)/6-31G** calculations have been done only at the peaks.
[b] Depends on the parameters of ARUPS measurements [8].

The full width at half maximum of the x ray used in the XPS experiments was about 1.5 eV [26], e.g., $\Gamma = 0.75$ eV. Using Eq. (2) with equal weight for the two curves, we obtain the corresponding line intensities described in Fig. 2(c). There is no other peak corresponding to the first ionization potential in Fig. 2(c) since its photoelectron cross section is diffuse. This agrees well with both the XPS and UPS spectra, in which no peak around the IP in Fig. 2(a) was observed.

The measured shoulder in XPS, labeled I_s in Table I, was originally erroneously thought [3,10] to be the IP, but, instead, is the result of overlap among the I_1, I_2, and the IP peaks. The enlarged part in Fig. 2(c) clearly shows that there is a shoulder in the MBPT(2) spectrum when Γ is 0.75 eV. The shoulder located at about 9.5 eV agrees well with the XPS results of 9.6 and 9.8 eV. The shoulder appears in the photoelectron spectrum only when the relative photoelectron cross sections of the two bands corresponding to C_{2p} and H_{1s} bonding have a suitable ratio. Because of this unfavorable ratio, the shoulder could not be seen in most UPS spectra [8]. However, if one checks the measured spectra carefully, one can discern the shoulder in the spectra observed at special angles and energies.

Although the IP cannot be accurately measured in either the XPS or UPS experiments, since the radiation width is not small enough, it can be deduced from the measured energy gap and the work function. The IP value determined by Delhalle *et al.* [3] in this way for polyethylene was 8.3 eV. The work function used in his determination was 4.5 eV. To match with the other experimental data given by Seki *et al.* [8], the experimental IP, namely 8.6 eV, listed in Table I is determined by taking the work function to be 4.8 eV deduced from the ARUPS experiments. Our MBPT(2) IP with basis set 6-31G** is 8.4 eV, which agrees well with the experimental result.

In both the XPS and UPS spectra, the two peaks corresponding to I_1 and I_2 are too close to be distinguished, so only one peak is observed with any given experimental parameters. As mentioned for I_s above, the relative photoelectron cross sections of the two peaks vary differently with the incident angle of the radiation, the energy of the radiation, and the emission angle of the electrons. The maximum corresponding to I_1 and I_2 in the photoelectron spectra varies between I_1 and I_2 with the three parameters. It could be larger than I_2 since the DOS at the outside of I_2 is very large. The position of the peak measured in the ARUPS experiment, indeed, varies from 10.5 to 12.0 eV with the experimental parameters [8]. Considering our MBPT(2) values for I_1 and I_2 with basis set 6-31G** are 10.59 and 11.06 eV, respectively, the agreement between theory and experiment is excellent. Since the three parameters in the XPS experiment are fixed, only one peak is observed for I_1 and I_2, which occurs at 11.1 and 11.2 eV in the two XPS measurements, respectively, again in excellent agreement.

The peak I_x measured in an earlier XPS experiment [3] was not observed in the later XPS spectra [4] and the ARUPS measurements [7]. The MBPT(2) ionization spectrum in Fig. 2(c) supports the later experiments, indicating the I_x peak to be an artifact.

For the peaks I_3 and I_4, the MBPT(2) values agree closely with those observed in the three experiments. Peak I_4, as shown in Fig. 2(c), is at the foot of the much stronger peak II_1. It is easily suppressed by the tail of II_1 if the signal-to-noise ratio is not adequate. This is probably why I_4 was not observed in the earlier XPS experiment [3] while it was in others [4,8].

The two energetic peaks II_1 and II_2 come from the C_{2s} bonding band. II_1 has two peaks in the spectrum of the DOS described in Fig. 2(a). The peaks are so close that only one peak could be observed in the XPS and UPS experiments, as happened for the two peaks corresponding to I_1 and I_2. However, since the two peaks of II_1 belong to the same band, the relative photoelectron cross sections of the two peaks vary in the same pattern with the two angles and the radiation energy in the ARUPS measurements. Thus, the position of the peak should not vary much with these experimental parameters. This is why a peak with a stable position for II_1 was observed while the peak for I_1 and I_2 varied over a range in the ARUPS measurements [8]. Once again, our MBPT(2) results agree well with those observed in the XPS and ARUPS experiments.

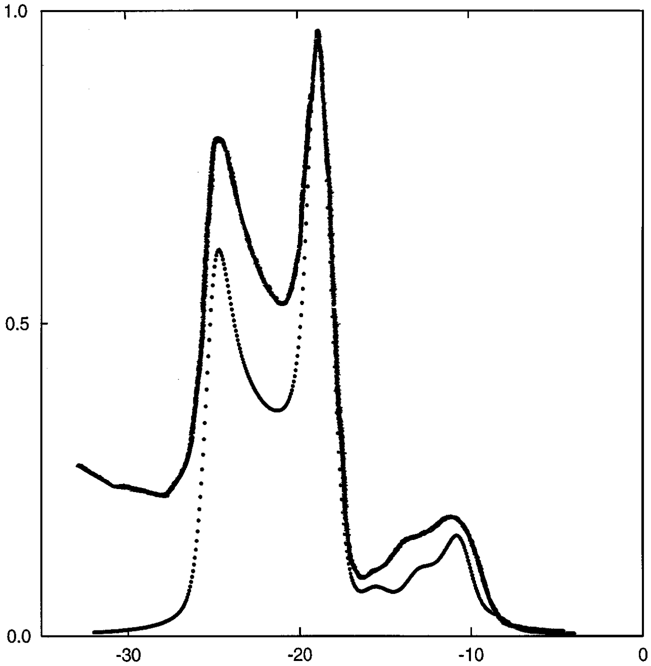

FIG. 3. Comparison between the experimental and the MBPT(2) XPS for polyethylene. Solid line: experimental XPS measured by Pireaux *et al.* [4b]; circles: the MBPT(2) photoelectron spectra shown in Fig. 2(c).

For the II_2 peak, the three experimental values are 23.6, 23.8, and 24.6 eV, respectively, differing by 1 eV. Our MBPT(2)/6-31G** value is 24.66 eV, which is in excellent agreement with that of the ARUPS measurement, believed to be the most reliable [8].

A direct comparison between the MBPT(2) photoelectron spectra shown in Fig. 2(c) and the experimental XPS spectra measured by Pireaux *et al.* [4(b)] is given in Fig. 3, where the II_1 peak of the two spectra has been superimposed. The two spectra match very well, even including the three small peaks that fall between -10 and -16 on Fig. 3.

In conclusion, we have obtained the quasiparticle band energies for the three valence bands of polyethylene using correlated [MBPT(2), 6-31G, 6-31G**] *ab initio* theory for extended systems. Unlike HF or DFT (LDA and BLYP) calculations, MBPT(2) accurately explains the XPS and UPS measurements while also resolving the discrepancies among the experiments. Further work will focus on higher order CC/MBPT and two and three dimensional systems.

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