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Electronic spectra of finite polyenes and polyacetylene obtained by electron and polarization propagator calculations*

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Summary. Polyacetylene and the short polyenes are used as common test cases for demonstrating the capability of electron and polarization propagator theory to simulate various types of molecular electronic spectra.

Key words: Propagator theory – Electron propagators, polarization propagators – Polyenes – Polyacetylene – Molecular electronic spectra

1. Introduction

Quantum molecular simulations have progressed along different, competing and complementing, lines of development. From the focus on total energies and molecular gradients, the development now directs towards molecular properties and spectra in general. Implementations of advanced propagator methods have been instrumental in the late efforts, and have found applications on a wide range of molecular phenomena. Jan Linderberg was one of the early originators of propagators in the context of quantum molecular science, and much of the ongoing work in this area has been inspired by his pioneering contributions and by the "yellow book" [1]. As we hope to indicate with the present contribution, propagator methods stood the test over the years and the challenge to theory and computations posed by the experimental progress, in this work represented by molecular electron spectroscopies, has been met.

In the present work we intend to show the performance and possibilities of current propagator implementations with respect to calculations of molecular electronic spectra. This includes applications of both electron and polarization propagators, viz. Auger, double charge transfer, X-ray emission, X-ray absorption and photoelectron spectra in the first case, and one- and two-photon absorption and single–triplet excitation spectra in the second case. The characteristics of these applications are best displayed by choosing a common set of samples, and we choose here polyacetylene and the short polyenes, viz. ethylene, butadiene, hexatriene and octatetraene, for this purpose. The polyenes are frequently used as test compounds for a variety of methods addressing properties of oligomers. They

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* Dedicated to Jan Linderberg on his 60th birthday

provide good test cases for the convergence behaviour of oligomeric properties, for size extensivity and role of long-range interactions for the electronic spectra, and for the applicability of building block models which relate spectroscopic features with local electronic structures. Systematic theoretical studies of the excited states of these molecules have been presented by state-specific methods such as multireference determinant configuration interaction methods [2–4], and by propagator-oriented methods as reviewed here. The latter have, in addition to electronic spectra, also allowed simulations of various types of molecular properties. A development towards larger molecules has recently taken place for calculations of one- and two-photon spectra using direct atomic orbital techniques [5], which has enabled the application on larger molecules than otherwise would have been possible. Concerning methods for long polymer-like chains it may be mentioned that long finite alkane chains have also been treated on a correlated *ab initio* level by a modification of the matrix-block negative-factor-counting method [6]. However, because of the comparably small amount of applications of these methods yet available, we restrict the present review to the short polyenes on the one hand, and to the extended systems with periodic boundary conditions, here polyacetylene, on the other.

2. General theory

2.1 Propagator methods for systems of different size

Propagator or Green's function methods are traditionally used in quantum chemistry when a direct approach to transition energies and moments of spectra is sought. When propagators methods were introduced in quantum chemistry in the 1960s, the first efforts of actual calculations were concentrated mainly on the particle–hole propagator and the related polarization propagator. Initially used in connection with semiempirical approaches, e.g. for alternant hydrocarbons [7, 8], the particle–hole propagator for molecules was soon implemented by *ab initio* methods at different levels of approximation. During the time of semiempirical calculations, the one-particle propagator seems to have served the somewhat indirect use of providing a renormalization of the particle–hole propagator [7, 8]. The one-particle propagator for finite electronic systems did, however, receive a renewed interest when its own perturbation expansion was employed in *ab initio* calculations of ionization potentials of atoms [9, 10] and molecules [11]. It was important in this development that breakdown effects in molecular photoelectron spectra were made accessible by means of one-particle Green's function calculations [12]. It may be added that one-particle propagator calculations can also provide information on other than photoelectron spectra. We will exemplify this for X-ray emission and absorption spectra in Sections 3.3 and 3.4. Another propagator we are interested in is the particle–particle Green's function which has found quantum chemical applications in *ab initio* calculations of Auger and DCT (double charge transfer) spectra of molecules as will be outlined in Section 3.2. Polarization and particle–hole propagator calculations will be discussed in Section 3.5. The above propagators (one-particle, particle–hole, particle–particle) have also been applied in *ab initio* calculations of several spectral properties of polymers, with similar methods as those in use for molecules. We intend a discussion of these various spectroscopies for finite and infinite polyenes under the unifying aspects of propagator theory.

In addition to providing a direct approach to many spectra, propagator methods also have other advantages. One point to be mentioned is that they allow for useful partial summation techniques which may be described as appropriate selection of classes of diagrams. For example, renormalization of the one-particle lines occurring in the two-particle propagator yields a connection of Auger and DCT spectra to photoelectron spectra. Another point important for our purpose is that the perturbation expansions of propagator theory ensure size-extensivity which makes a unified treatment of finite and infinite systems possible. The size-extensivity (or size-consistency) requirement of a method means that the quality of the results, in a given approximation, should not depend on the system size. This property, which is by construction guaranteed for Green's function methods [13–16], in contrast *inter alia* to configuration interaction methods [17], qualifies them as ideal tools for the purpose of investigating the oligomer to polymer transition for polyenes. Considering the computational effort when studying systems of increasing size, it may become important to have methods which can also describe a quasi-continuous manifold of states. Propagator methods for time-independent systems typically yield all the energy differences and transition moments for a spectrum in one single calculation. This may form a basis for developing methods which include correlation effects when calculating histograms of the density of quasi-particle states for very large polymer-like molecules [6].

Polyacetylene represents the infinite-size limiting case of polyenes. This case is computationally accessible by exploiting the translational symmetry of the periodic system. At the level of the Hartree–Fock approximation this is reflected in the crystal-orbital equations [18–20] which yield the electronic band structure of the polymer. Corrections of the Hartree–Fock results to account for electronic correlation at the *ab initio* level can provide quasi-particle shifts for some of the bands. For example, the fundamental band gap has been obtained in this way. The calculation of these shifts has been achieved by Møller–Plesset perturbation theory based on the Rayleigh–Schrödinger expansion up to second order [21]. A third-order calculation of the quasi-particle shifts for polyacetylene has been performed [22] by means of the Dyson equation of Green's function theory. The spectral density of the one-particle Green's function for the whole valence region has been calculated with a second-order irreducible self-energy part and several correlation effects have been considered [23, 24]. Exciton binding energies of polyacetylene have also been calculated by propagator or propagator-related methods [25, 26, 22]. Applications of the one-particle Green's function to the calculation of X-ray spectra of polacetylene and of the particle–particle propagator to the calculation of the Auger spectrum of polyacetylene will be discussed in Section 3.

2.2 *Definition of propagators for molecules and polymers*

A general double-time Green's function appropriate for the present purposes may be defined as follows [1, 27, 28]:

$$\langle\langle A;B\rangle\rangle_\omega = -\mathrm{i}\int_{-\infty}^{\infty} \mathrm{d}t\,\mathrm{e}^{\mathrm{i}\omega t}\langle \Psi_0 | T\{\hat{A}(t)\hat{B}(0)\} | \Psi_0\rangle, \tag{1}$$

where Ψ_0 is the correlated ground state of the neutral molecule, and T is Wick's time ordering operator. By $\hat{A}$ and $\hat{B}$ we denote the Heisenberg representation of the time dependence of the operators A and B induced by the adiabatic switching of a part of the Hamiltonian. It is useful to consider special operators A and B of a given particle rank, namely one-particle operators, particle–hole, two-particle, three-particle operators, etc. We will collect the double-time Green's functions obtained in this way under the concept of electron propagators. A double-time Green's function where A and B are general number-conserving one-electron operators is called a polarization propagator. By inserting the second-quantization expressions for A and B the polarization propagator may be expanded in terms of particle–hole propagators.

The spectral resolution of a double-time Green's function, the Lehmann representation, is given by

$$\langle\langle A;B\rangle\rangle_\omega = \sum_f \frac{\langle \Psi_0|A|\Psi_f\rangle\langle \Psi_f|B|\Psi_0\rangle}{\omega + E_0 - E_f + \mathrm{i}\eta} - \sum_{f'} \frac{\langle \Psi_0|B|\Psi_{f'}\rangle\langle \Psi_{f'}|A|\Psi_0\rangle}{\omega + E_{f'} - E_0 - \mathrm{i}\eta}, \tag{2}$$

where η is a positive infinitesimal tending to zero in the distributional sense and the sums extend over the final states Ψ_f and $\Psi_{f'}$ reached by operation of A and B, and E_f and $E_{f'}$ are the corresponding energies.

If A is an observable of the system and B is an operator describing a perturbation, then the retarded polarization propagator for this case is identical to the linear response function [29]. Its spectral representation is

$$\langle\langle A;B\rangle\rangle^r_\omega = \sum_f \frac{\langle \Psi_0|A|\Psi_f\rangle\langle \Psi_f|B|\Psi_0\rangle}{\omega + E_0 - E_f + \mathrm{i}\eta} - \sum_{f'} \frac{\langle \Psi_0|B|\Psi_{f'}\rangle\langle \Psi_{f'}|A|\Psi_0\rangle}{\omega + E_{f'} - E_0 + \mathrm{i}\eta}. \tag{3}$$

This formally differs from Eq. (2) in the position of the poles in the complex plane.

Several notations are in use for the different electron propagators. For convenience, we will also employ the following:

$$G_{kl}(\omega) = \langle\langle a_k; a_l^+ \rangle\rangle_\omega \tag{4}$$

(the one-particle propagator),

$$\mathcal{G}_{klmn}(\omega) = \langle\langle a_l a_k; a_m^+ a_n^+ \rangle\rangle_\omega \tag{5}$$

(the particle–particle propagator),

$$\mathcal{P}_{klmn}(\omega) = \langle\langle a_l^+ a_k; a_m^+ a_n \rangle\rangle_\omega \tag{6}$$

(the particle–hole propagator).

These propagators have the special form $\langle\langle X_k; X_l^+ \rangle\rangle$ where X_k and X_l are operators of the same particle rank, distinguished only by the actual value of the indices k and l. The indices must be both of the same kind which may be one-particle, particle–hole or two-particle (two-hole) indices. The Lehmann representation, Eq. (2), then becomes:

$$\langle\langle X_k;X_l^+\rangle\rangle_\omega = \sum_f \frac{\langle \Psi_0|X_k|\Psi_f\rangle\langle \Psi_f|X_l^+|\Psi_0\rangle}{\omega + E_0 - E_f + \mathrm{i}\eta} - \sum_{f'} \frac{\langle \Psi_0|X_l^+|\Psi_{f'}\rangle\langle \Psi_{f'}|X_k|\Psi_0\rangle}{\omega + E_{f'} - E_0 - \mathrm{i}\eta}. \tag{7}$$

The poles are $\omega_f = E_f - E_0$ and $\omega_{f'} = E_0 - E_{f'}$, i.e. the ionization potentials (IPs) and electron affinities (EAs) for the one-particle propagator, the double ionization potentials (DIPs) and double electron affinities for the particle–particle propagator and the excitation energies for the particle–hole propagator (and thus also for the linear response functions).

The residues are

$$\mathrm{res}_{\omega_f}\langle\langle X_k;X_l^+\rangle\rangle = \langle\Psi_0|X_k|\Psi_f\rangle\langle\Psi_f|X_l^+|\Psi_0\rangle \tag{8}$$

and

$$\mathrm{res}_{\omega_{f'}}\langle\langle X_k;X_l^+\rangle\rangle = \langle\Psi_0|X_l^+|\Psi_{f'}\rangle\langle\Psi_{f'}|X_k|\Psi_0\rangle. \tag{9}$$

It is useful to define a correlation factor for the corresponding spectra by

$$\chi_k = \langle\Psi_f|X_k|\Psi_0\rangle. \tag{10}$$

This quantity is a factor in the above residues of the propagator $\langle\langle X_k;X_l^+\rangle\rangle$. It is also accessible by wave function methods and its behaviour for different levels of electron correlation effects will be discused in Section 2.3. Furthermore, it will be shown in Section 3 how these different levels of electron correlation effects turn up in the various spectra in terms of the correlation factors.

The polymer case differs from the molecular treatment firstly by an additional k-dependence of the indices. The indices are usually composed of band and quasi-momentum indices referring to the canonical polymer orbitals which are assumed to have the following form [19, 20]:

$$\phi_j(k) = N^{-1/2}\sum_{H\mu} \mathrm{e}^{ikR_H} c_{\mu j}(k)\chi_\mu, \tag{11}$$

where k is the quasimomentum, H the cell index and N the number of unit cells. The limit $N \to \infty$ is then performed in the integrated expressions and yields the quasi-continuous k-dependence.

2.3 Classification of correlation phenomena

One can distinguish several different levels of electron correlation effects by considering different cases for the correlation factors introduced above. In this way one can identify the approximations which lead from Koopmans theorem and the quasi-particle picture to hole-mixing and breakdown effects. These phenomena are of a quite general nature and hold both for electron and polarization propagators, but have received most attention in the applications of electron propagators (one-particle- and particle–particle-) on photoelectron- [30] and Auger [31] spectroscopy. There are essentially the following five levels of electron correlation, as we refer to in the sections to come:

1. One χ_k is equal to 1, the others are zero. In terms of Green's functions this means: $\mathrm{res}\langle\langle X_k;X_l^+\rangle\rangle = \delta_{kl}\delta_{kp}$ for a particular (one-particle, particle–hole or two-particle) index p. The Hartree–Fock picture is retained which implies that the energetics of the spectrum has to be analysed by Koopmans theorem, and intensities by the MO factor τ_k alone (see definitions in Eqs. (19), (33) and (39)). This in turn can be conducted in terms of MO theory, local densities, effective and strict selection rules as further demonstrated in Section 3.

2. One χ_k is close to 1, the others are close to zero. In terms of Green's functions: res $\langle\langle X_k;X_k^+\rangle\rangle$ is close to 1 for a particular index k. The quasi-particle picture holds. The energetics is considerably improved on Koopmans theorem. An MO analysis is still possible.

3. More than one χ_k enters in the wave function. In most cases this would also mean that these χ_k factors are present in more than one state. In terms of Green's

functions: More than one $\langle\langle X_k; X_k^+\rangle\rangle$ enters in the residues. This situation is referred to as hole mixing, leading to electronic interference in the transition cross sections.

4. One single χ_k is large, but occurs in several states. In terms of Green's functions: One $\langle\langle X_k; X_k^+\rangle\rangle$ occurs strongly in the residues of several poles. One can then not associate a 1–1 correspondence between pairs of MO:s (or MO factors) and spectral bands (states). Therefore, one can speak of a complete breakdown of the molecular orbital and the quasi-particle pictures in this case.

5. No single χ_k is large. In terms of Green's functions: No single $\langle\langle X_k; X_k^+\rangle\rangle$ has a large contribution to the residue of a certain pole. Such states are called correlation state satellites.

3. Special spectroscopies

3.1 Photoelectron spectra

Photoelectron spectra represent one of the conceptionally simplest probes of the electronic structure of molecules and polymers. This is because they are essentially one-hole spectra. The appropriate propagator for their calculation is the one-particle Green's function. Ultra-violet and X-ray photoelectron spectra (UPS and XPS) emphasize different valence regions, namely the outer, respectively, inner valence regions. XPS spectra of polyenes and polyacetylene show evidence of strong correlation phenomena [32]. For the polyene oligomers several calculations have predicted these effects [33, 34, 30]. In terms of the correlation scheme given in the previous section they can be classified as breakdown effects. In the molecular case this has already been discussed several times [30]. Here we want to turn our attention to the fact that such effects are also predicted by one-particle propagator calculations on the complete valence region of polyacetylene [23, 24].

In the polymer case the spectral density of the advanced part of the one-particle propagator has been evaluated as a quasi-continuous sum extending over the occupied bands:

$$A^-(\omega) = \sum_{I,\mu}^{\text{occ}} P_{I\mu}\delta(E - \omega_{I\mu}), \tag{12}$$

where the index $I = (i, k)$ comprises band indices i and quasi-momentum k, μ enumerates the satellite bands, and $\omega_{I\mu} = \omega_{i\mu}(k)$ the pole strengths of the one-particle propagator.

The poles are calculated from the inverse Dyson equation. Since the one-particle Green's function is diagonal in the k-indices, the Dyson equation can be written as a matrix equation over band indices only, but having a parametrical k-dependence:

$$\boldsymbol{G}^{-1}(k,\omega) = \boldsymbol{G}^{(0)-1}(k,\omega) - \boldsymbol{M}(k,\omega), \tag{13}$$

where $\boldsymbol{G}^{(0)-1}$ is the inverse diagonal matrix of the interaction-free one-particle Green's function, the elements of which are

$$G_{ij}^{(0)-1}(k,\omega) = (\omega - \varepsilon_i(k))\,\delta_{ij} \tag{14}$$

and $\boldsymbol{M}$ is the matrix of the irreducible self-energy part in second order:

$$\begin{aligned} M_{pq}(k,\omega) = \sum_{JKL} & V_{PJKL}(2V_{KLQJ} - V_{KLJQ}) \times \delta_{(k+k_j)(k_k+k_l)} \\ & \times \{ n_J \bar{n}_K \bar{n}_L (\omega + \varepsilon_J - \varepsilon_K - \varepsilon_L + i\eta)^{-1} \\ & + \bar{n}_J n_K n_L (\omega + \varepsilon_J - \varepsilon_K - \varepsilon_L - i\eta)^{-1} \} \end{aligned} \tag{15}$$

where n_J are the occupation numbers ($\bar{n}_J = 1 - n_J$), and V_{IJKL} are the two-electron integrals.

The residues of the one-particle propagator are obtained as

$$\mathrm{res}_{\omega_{I\mu}} \langle\langle a_k; a_l^+ \rangle\rangle = P_{I\mu} |c_{JI\mu}|^2, \tag{16}$$

where $c_{JI\mu}$ is the Jth component of that eigenvector of G^{-1} which belongs to the eigenvalue having a zero at $\omega_{I\mu}$. The pole strength is obtained as

$$P_{I\mu} = \left(1 - \left[\frac{\mathrm{d}M_{I\mu}}{\mathrm{d}\omega} \right]_{\omega_{I\mu}} \right)^{-1}, \tag{17}$$

where $M_{I\mu}$ is the eigenvalue of $\boldsymbol{M}$ corresponding to the above eigenvalue of $\boldsymbol{G}$.

The results of the calculations in ref. [24] show that breakdown effects are responsible for the structures between 22 and 34 eV, related to the vacuum level, (or between 17 and 29 eV related to the Fermi level) in the XPS spectrum of polyacetylene. In particular the 3σ band is split into several components. At the origin of the Brillouin zone the splitting amounts to almost 1 eV, and the largest polestrength at this point is only 0.25. Hole mixing occurs between the 5σ and 6σ bands at the end points of the Brillouin zone ($k = \pi/a$ and $k = -\pi/a$), but the admixtures are weak (the residues enter the pole strengths in a 0.06:0.41 ratio).

The correlation corrections in the outer-valence region of polymers may be understood in terms of the electronic polaron model of solids [35, 36], which essentially just shifts the quasi-particle bands to lower binding energies. The mechanism in the innervalence region is analogous to that observed for finite molecules [30] and is due to an interaction of one-hole states with energetically close-lying one-particle-two-hole states. The appearance of these effects is dependent on the specific system. For example, there is no breakdown of the quasi-particle picture for polyethylene.

3.2 Auger and DCT spectra

A direct approach to the calculation of Auger and DCT (double charge transfer) spectra of molecules and polymers is provided by methods based on the particle–particle propagator or particle–particle Green's function. This function was first introduced within the context of electron gas theory [37], and has later been applied to solid-state Auger spectra, e.g. Auger spectra of narrow-band metals [38]. The particle–particle Green's function has also been employed in *ab initio* calculations of Auger spectra of finite molecules [39]. Further developments of these methods will be discussed below and have recently been reviewed in length in Ref. [31].

In the context of Auger spectra the relevant features of these methods are the following: The poles of the particle–particle Green's function, the double-ionization potentials, determine the position of the Auger lines on a binding energy scale. The residues of the particle–particle Green's function yield the correlation factors modulating the matrix elements in the calculation of transition rates. The statement for the poles follows immediately from the Lehmann-representation in Section 2.1. The role of the residues is easily displayed by using a result of Manne and Ågren [40] who evaluated the Auger transition rates from initial state Ψ_i to final state Ψ_f within Wentzel's ansatz. By imposing the single-channel and strong-orthogonality conditions to their general result they found that the rates in many cases of interest (e.g. K–LL transitions with frozen 1s orbitals) can be given in a simple form, namely:

$$W_{fi} = \left| \frac{1}{2} \sum_{qrs} \tau_{qrs} \chi_{qrs} \right|^2 , \tag{18}$$

where the incoherent sum over the possible channels is implicitly assumed (referred to by the index u for the continuum orbital below) and

$$\tau_{qrs} = V_{uqrs} - V_{uqsr} \tag{19}$$

is called the molecular orbital factor and

$$\chi_{qrs} = \langle \Psi_f | a_q^+ a_r a_s | \Psi_i \rangle \tag{20}$$

the correlation factor.

Because of the almost perfect orthogonality between states with holes in different core orbitals or with holes in core and valence orbitals, it is motivated for all practical purposes to limit in the above expression the index q to one ($q = c$) to describe the core hole. Thus

$$\chi_{qrs} = \langle \Psi_f | a_r a_s | \Psi_0 \rangle \tag{21}$$

and W_{fi} becomes the sum of the residues of the particle–particle Green's function $\mathscr{G}_{klmn}$ modulated by the orbital factors [41]:

$$W_{fi} = \frac{1}{4} \sum_{klmn} \tau_{clk} \tau^*_{cnm} \operatorname{res}_{E_f} \mathscr{G}_{klmn} . \tag{22}$$

The classification scheme of correlation effects of Section 2.3 applies to the above correlation factors. It may be noted that the analysis is usually further simplified by also decomposing the molecular orbital factor τ_{clk} in a linear combination of contributions from atomic orbitals and invoking the one-center intensity model [42].

Diagram summation of the Feynman–Goldstone expansion of $\mathscr{G}_{klmn}$ yields the Bethe–Salpeter equation which in defined cases may be cast into a factorizable matrix form. The terms appearing in the Bethe–Salpter equation and defining the corresponding sets of approximations are the irreducible vertex part K and the (renormalized) interaction-free two-particle Green's function $\mathscr{G}^{(0)}$. These terms can be interpreted as describing the interaction of the two holes with each other or with the rest of system, respectively.

More explicitly, the Bethe–Salpeter equation determines the matrix of $\mathscr{G}^{-1}$:

$$\mathscr{G}^{-1}(\omega) = \mathscr{G}^{(0)-1}(\omega) - \mathscr{K}, \tag{23}$$

where the elements of the first-order irreducible vertex part are given by

$$\mathscr{K}^{(\mathrm{S,T})}_{klmn} = V_{klmn} + / - V_{klnm} \quad \text{if } k < l \text{ and } m < n, \tag{24}$$

$$\mathscr{K}^{(\mathrm{S})}_{klmn} = V_{klmn} \quad \text{if } k = l \text{ and } m = n, \tag{25}$$

$$\mathscr{K}^{(\mathrm{S,T})}_{klmn} = \sqrt{2} V_{klmn} \quad \text{if either } k = l \text{ or } m = n. \tag{26}$$

The different signs refer here to singlets (S) or triplets (T). In the second order of the irreducible vertex part, not considered here, the two-particle integrals enter quadratically and energy denominators appear [43].

The renormalized interaction-free particle–particle Green's function $\mathscr{G}^{(0)}$ is given by

$$\mathscr{G}^{(0)}_{klmn}(\omega) = \gamma_{kl}\delta_{km}\delta_{ln}\sum_{\mu\nu}\frac{P_{k\mu}P_{l\nu}}{\omega - \omega_{k\mu} - \omega_{l\nu}}, \tag{27}$$

where $\omega_{k\mu}$ are the poles of the one-particle Green's function, $P_{k\mu}$ the corresponding residues and γ_{kl} is -1 if k and l refer to occupied orbitals, $+1$ if they refer to unoccupied orbitals and zero otherwise.

To determine the poles of $\mathscr{G}$ one can solve for the zeros of the eigenvalues of $\mathscr{G}^{-1}$ from the Bethe–Salpeter equation. For practical calculations the above pole-search problem may be conveniently transformed into an eigenvalue problem. The price to be paid is that the dimension of the matrices even with first order vertex part is already larger than that of a two-particle-RPA because of the possible combinations of additional (non-quasi-particle) poles of the one-particle Green's function.

In this approximation hole mixing is mediated through the irreducible vertex part and breakdown effects enter through the renormalized interaction-free two-particle Green's function which contains the poles and residues of the one-particle Green's function. The one-particle data can be compared to photoelectron spectra and it is thus possible to trace down how breakdown phenomena in the photoelectron spectrum influence Auger spectra.

In addition to the Bethe–Salpeter equation other approximation schemes for the particle–particle Green's function have been developed. On the one hand they are derived by the algebraic diagrammatic construction (ADC) scheme [34] and effective Hamiltonian transformation techniques [44], on the other by the superoperator resolvent representation of the particle–particle Green's function [45] and multiconfigurational versions theoreof [46]. These different treatments of the two-particle Green's function will in general lead to other levels of approximation than defined above in the context of the Bethe–Salpeter equation. There are, however, some simple approximations (e.g. the Tamm–Dancoff approximation) which are obtained as the first steps in all these formulations.

In the polymer case the Bethe–Salpeter equation can be transformed to the following form [47] which is analogous to the exciton representation of the particle–hole propagator:

$$\tilde{\mathscr{G}}^{-1}(K,\omega) = \tilde{\mathscr{G}}^{(0)-1}(K,\omega) - \tilde{\mathscr{K}}(K), \tag{28}$$

where the transformed matrices in the mixed representation have cell and two-hole indices. They are given by

$$\tilde{\mathscr{G}}^{0}_{s'i'j'sij}(K,\omega) = \gamma_{ij}\delta_{i'i}\delta_{j'j}\frac{1}{2\pi}\int_{-\pi}^{\pi}\mathrm{d}k\exp(\mathrm{i}k(R_{s'} - R_s))\sum_{\mu\nu}\frac{P_{i\mu}(k)P_{j\nu}(K-k)}{\omega - \omega_{i\mu}(k) - \omega_{j\nu}(K-k)}, \tag{29}$$

where s' and s are the cell indices, $\omega_{i\mu}(k)$ the quasi-particle bands and $P_{i\mu}$ the pole strengths, and

$$\tilde{\mathscr{K}}_{s'i'j'sij}(K) = \sum_{u}\exp(\mathrm{i}KR_u)\mathscr{K}^{w}_{i'j'ij}(u+s', u, s, 0) \tag{30}$$

where $\mathscr{K}^w$ is the irreducible vertex part taken with Wannier functions centred at the cells given in the four arguments. Therefore, finding well-localized Wannier functions is important for keeping the computational effort within limits. Several procedures for localizing Wannier functions by appropriate variation of the phase factors of the Block functions have been suggested [21, 48].

The localization properties of the Auger final states in the first oligomeric members of the polyacetylene sequence have been analysed by the particle–particle Green's function method in order to extrapolate the dicationic states of the oligomers to corresponding final states of the Auger process in polyacetylene [49]. Band shape formation and the localization properties of the Auger final states in an infinite system are topics of interest in this context.

An unsaturated hydrocarbon system is expected to display considerable correlation effects. For polyacetylene this has been evidenced in terms of breakdown effects in the photoelectron spectrum both experimentally [32] and theoretically [24]. The calculations [49] predict strong hole-mixing effects in the low binding energy region of the Auger spectra of polyacetylene. It is possible to relate these to corresponding effects in the Auger spectra of butadiene and hexatriene where they lead to observable sharp peaks [49].

In butadiene the highest occupied $1b_g$ orbital is a combination of the two left-hand carbon p_z atomic orbitals and of the two right-hand carbon p_z's with opposite sign, but equal magnitude of the components. In contrast, the next highest occupied orbital, $1a_u$, is a combination of the carbon p_z orbitals with qualitatively similar magnitude of the components as in the HOMO, but equal sign for all four carbon p_z orbitals. State interference leads to two states in this case, one where the $1b_g$ double-hole configuration essentially is mixed with the $1a_u$ double-hole configuration with opposite sign and mixing coefficients of the same order of magnitude, and one where the two configurations enter with equal sign. In the first case the final state contains mainly contributions where the two holes are located at different sides of the molecule, in the second case the main contributions have the holes at the same side of the chain. Naturally, hole–hole interaction is smaller in the first case than in the second case, so the state appears at lower binding energy (26.39 eV) than the other (31.88 eV). The coupled site-selectivity leads to lower intensity in the first case than in the second. A corresponding situation exists in hexatriene: The highest occupied orbital is $2a_u$ and has p_z components with equal sign at both sides of the chain, whereas the next orbital, $1b_g$, has a change in sign across the middle of the molecule. Again, the two-hole configurations from these two orbitals lead to two states, the first at 21.51 eV binding energy describing the delocalized case and being responsible for the first peak on the low binding energy side of the spectrum. The second describes the case where the two holes move at the same side and, being situated at 25.70 eV binding energy, contributes to the second peak in the spectrum.

The above-described scenario remains valid for polyacetylene. The only difference is that the completely delocalized states do not appear in the polymer spectrum because there they cannot carry intensity. Thus the onset of intensity in the calculated polymer spectrum [49] is determined by those states only which represent a coupled motion of the two holes within each other's vicinity. In contrast to saturated hydrocarbon chains, the polyacetylene spectrum is largely dominated by outer–outer valence double-hole states.

Compared to other spectroscopies, band formation in the Auger lineshape should be fast because of the local probe character of this spectroscopy. For the oligomers of the polyacetylene sequence considered here, however, convergence of the lineshape was not reached up to hexatriene as can be evidenced by comparison of the calculated oligomer spectra with the calculated polyacetylene spectrum. This behaviour must be considered to be a consequence of the slow convergence of the lattice sums for polyacetylene. It is typical for a low-gap semiconductor and stands in contrast to the situation in insulating polymers like polyethylene. In the latter case it is known that the convergence of the alkane Auger lineshapes to that of polyethylene is comparatively fast [50, 23].

3.3 X-ray emission spectra

We have applied an *ab initio* one-particle propagator method to the calculation of X-ray emission spectra (XES) of finite and infinite polyenes [51]. The method was derived from a two-step formulation of the X-ray emission process, aiming at a tractable computational scheme for these systems. The approximations which lead from a one-step description, starting out from multi-channel resonance scattering theory, to two-step models, separating deexcitation from excitation, are in principle known [52–55]. Provided that X-ray emission can be treated within the two-step model for electron–molecule or photon–molecule inelastic scattering, with core excitation and decay separated, the X-ray spectral rates can be analysed starting out from Fermi golden rule like expressions. In relative units these take the form:

$$W_{cf} \simeq E^3 |\langle \Psi_i | D | \Psi_f |^2 = E^3 \left| \sum_x \tau_x \chi_x \right|^2, \tag{31}$$

where Ψ_i and Ψ_f are, respectively, the core ionized and valence ionized initial and final states in the $N - 1$ electron system. The rate is thus expressed as a sum of terms, each of which constitutes a product of a molecular orbital (MO) factor τ_x and a many-body factor χ_x. The slowly varying energy factor preceding this expression is omitted for simplicity. In X-ray emission x stands for a double index p, q, because the many-electron dipole operator D is written

$$D = \sum_{p,q} \langle \phi_p | d | \phi_q \rangle a_p^+ a_q, \tag{32}$$

where d is the one-electron dipole operator, and $\{\phi_q\}$ and $\{\phi_p\}$ are sets of molecular orbitals that in general are mutually non-orthogonal.

The product of molecular orbital and many-body factors resolves as

$$\tau_x \chi_x = \langle \phi_p | d | \phi_q \rangle \langle \Psi_f(N-1) | a_p^+ a_q | \Psi_i(N-1) \rangle. \tag{33}$$

For all practical purposes, it is motivated to limit the index p to one, corresponding to the creation of a core hole at one specific site, $p = c$, due to the almost perfect orthogonality ($\chi_x \simeq 0$) between states with holes in different core orbitals or with holes in core and valence orbitals. For molecules with several core hole sites the result is a superposition of X-ray spectra each treated separately (different index p). The molecular orbital factor is defined by a common set of orthogonal molecular orbitals that can be optimized for any state involved in the X-ray emission process, but that in our computations always are defined by optimizing a single determinant wave function for the neutral ground state. With the two approximations given above, the truncation of the p index to one, referring to the core orbital, and the neglect of non-orthogonality (orbital relaxation), which is the critical approximation, the above expression is replaced by

$$\tau_x \chi_x = \langle \phi_c | d | \phi_q \rangle \langle \Psi_f(N-1) | a_q | \Psi_0(N) \rangle, \tag{34}$$

since under these assumptions the action of $a_q | \Psi_0(N) \rangle$ and $a_p^+ a_q | \Psi_i(N-1) \rangle$ is the same. The electronic factors are by definition the residues of the one-particle Green's function, $\mathrm{res}\, G_{kl}$, as defined in Section 2.1 above. Using the one-particle Green's propagator the X-ray rates are therefore given as

$$W_{cf} = \sum_{kl} \sum_{i}^{xyz} \langle \phi_l | d_i | \phi_c \rangle \langle \phi_c | d_i | \phi_k \rangle \, \mathrm{res}_{\omega_f} G_{kl}, \tag{35}$$

where ω_f is the pole corresponding to the final state ionization potential. Thus under the assumptions given above the Green's function analysis of the X-ray emission spectrum will be equivalent to the one for the (valence) photoelectron spectrum, only different MO factors are involved.

The energies of the emitted X-ray photons are obtained from the poles of the one-particle propagator, the ionization potentials, because

$$h\nu_X = IP_c - IP_f \tag{36}$$

where IP_c and IP_f denote the initial core and final valence state ionization potentials, respectively.

The above equations are related to the result obtained by Kondratenko, Gel'mukhanov et al. [56] by evaluation of the Kramers–Heisenberg relation for the cross section of inelastic resonance X-ray scattering. By invoking the two-step approximation for the process and considering only the second step, the core hole decay, we avoid calculation of the natural linewidth. Thus we assume the resonances in the cross section to be of the Dirac delta form and compare their positions to the local maxima of the experimental spectrum. Calculation of linewidths would require explicit consideration of the interaction with the continuum to take into account nonradiative (Auger) contributions in addition to the radiative linewidth.

The different cases for correlation effects described in Section 2.3 apply for the correlation factors in Eq. (35), and one recovers the approximations which lead from Koopmans theorem and the quasi-particle picture to hole-mixing and breakdown effects.

Using a one-centre decomposition of the orbital factor one obtains for the transition rates:

$$W_{cf} = \sum_{i,\mu,\nu} M_{c\mu}^{i} M_{c\nu}^{i*} \sum_{kl} c_{\mu l} c_{\nu l}^{*} \mathrm{res}_{\omega_f} G_{kl}, \tag{37}$$

where $M_{c\mu}^{i} = \langle \phi_c | d_i | \phi_\mu \rangle$ are the dipole matrix elements between the initial state core hole ϕ_c and the μth valence orbital. The x, y or z components of the dipole transition operator are here explicitly introduced by index i.

Similarly, one finds in the case of a polymer [51]

$$\begin{aligned} W_c(E) = \sum_{\mu\nu} \sum_{i}^{xyz} M_{c\mu}^{i} M_{c\nu}^{i*} \sum_{jlf} \int_{-\pi}^{\pi} \mathrm{d}k \int_{-\pi}^{\pi} \mathrm{d}k' \, \delta(E - \omega_f(k)) \\ \times c_{\mu j}(k') c_{\nu l}^{*}(k') \mathrm{res}_{\omega_f(k)} G_{jl}(k'). \end{aligned} \tag{38}$$

The calculations in [51] showed that the $2p$ localization that fingerprints the ethylene XES spectrum is gradually distorted in the process of delocalization. A problem is, while polyacetylene and the smallest subunit ethylene contains only topologically equivalent carbon atoms, all other members of the oligomer sequence contain nonequivalent carbon atoms. This leads to initial state chemical shifts that displace the accompanying X-ray emission transitions leading to a total spectrum of several overlapping core-sited sub-spectra. A recent study of the core electron chemical shifts [57] shows that there is a regular attenuating trend of end to bulk atom binding energies converging to the polyacetylene value, thereby displaying a quasi-one-dimensional analogue of surface to bulk chemical shifts. The effect of this on the X-ray emission spectrum is a gradual overall broadening going from ethylene to hexatriene, which turns into a sharpening as the "bulk" atoms with small shifts outnumber the end atoms with larger shifts.

It is found that band shape formation is slow in the X-ray emission spectra of the polyene sequence. This is expected from the results of other spectroscopies. It is interesting to compare with the situation in polyethylene: In the alkane sequence a single C 2*s* band starts to develop already in the *n*-butane photoelectron spectrum [58] and for the *n*-nonane photoelectron spectrum it is almost identical with that of polyethylene. Due to the Peierls distortion the dimerized unit cell of polyacetylene contains two nonequivalent carbon atoms. Therefore, two C 2*s* bands are formed for the polyenes considered here, namely one (3σ) between 24 and 29 eV and the other (4σ) between 17 and 24 eV. Furthermore, in polyacetylene the C 2*s* and C 2*p* regions are merging whereas they are clearly separated in poly-ethylene.

Since the orbital factor in the XES rate probes essentially the outer valence populations the XES intensity is stronger in the outer- than in the inner- valence energy range, compared to the polestrength of the one-particle Green's function in the molecular case or the spectral density of the one-particle Green's function in the polymeric case.

The resulting polyacetylene spectrum using the local probe character of XES appears to be rather ethylene-like [51]. It can be concluded that the molecule-like lineshape appearance for polyacetylene is not reached via formation of narrow bands: The highest valence band, (1π), is 7 eV broad, the next two (σ) C 2*p* bands are 3 and 4 eV broad respectively. Instead, the polymer peaks originate from the singularities of the density of states which almost coincide for the bottom of the highest and the top of the next valence band (6σ) around 12 eV [59, 24]. Furthermore, the bottom of the 6σ and the top of the 5σ band are together responsible for the structure around 14–15 eV, and the bottom of the 5σ band contribute to the structure at 16–17 eV, where the C 2*s* region (3σ and 4σ) starts. A site selectivity seems to emerge from a qualitative similarity of the discrete XES intensity distribution of the ethylene spectrum with the ratio of XES intensity to spectral density in the various parts of the polyacetylene spectrum. This can be interpreted as a manifestation of a local similarity of the correlated wave packets formed from the polymeric one-hole states in those energy regions to the corresponding molecular orbitals of the oligomeric subunits.

3.4 Near-edge X-ray absorption spectra

As in the case of X-ray emission we start out from the Fermi golden rule, Eq. (31), where Ψ_i and Ψ_f are now the neutral initial state and the core-to-bound excited final state of the N electron system, respectively. Proceeding as in Section 3.3 above, the NEXAFS rates resolve as

$$\tau_x \chi_x = \langle \phi_q | d | \phi_p \rangle \langle \Psi_f(N) | a_p^+ a_q | \Psi_0(N) \rangle \tag{39}$$

into a product of molecular orbital and many-body factors.

In the NEXAFS case it is justified to limit the index q to one, corresponding to the creation of a core hole at one specific site, $q = c$, due to the almost perfect orthogonality ($\chi_x \simeq 0$) between states with holes in different core orbitals or with holes in core and valence orbitals. This complies also in some sense with that simultaneous two-core sited spectra are not observed. The same arguments as in X-ray emission apply, only that we deal with an N- instead of an $N-1$ electron system and in that the core hole enters in the final instead of the initial state. For molecules with several core hole sites the result is a superposition of X-ray spectra (different index q) according to Eq. (39), which all can be treated separately. The molecular orbital factor is here computed out of one set of orthogonal molecular orbitals. In the X-ray emission case it is natural to choose the set of ground state canonical Hartree–Fock orbitals. For the NEXAFS case this set is not appropriate since its virtual orbitals are given by an N instead of an $N-1$ electron potential. We simulate here the removal of an electron from the N-electron potential by an addition of a proton, thus we optimize the set of orbitals by diagonalizing the equivalent cores ($Z + 1$) Fock matrix. For example, for ethylene the equivalent cores Fock matrix refers to $CH_2NH_2^+$. In doing so we neglect the core-virtual exchange interaction and thus singlet–triplet splitting in the NEXAFS spectrum. Since triplets are dipole forbidden all intensity is collected into the singlets and we still obtain the correct number of states in the Green's function calculation, although it yet neglects the core–virtual exchange. The core–virtual exchange two-electron matrix elements are generally small, only a few tenths of an eV, see e.g. work on carbonyl shake-up spectra in Ref. [60]. The application of the equivalent cores approximation also infers a localized, broken symmetry, solution for the core excitation process.

With the three approximations outlined above, viz. truncation of the p index to one, referring to the core orbital, the neglect of non-orthogonality (orbital relaxation) and the representation of the core hole system by its equivalent ($Z + 1$) core Eq. (39) is replaced by

$$\tau_x \chi_x = \langle \phi_c | d | \phi_p \rangle \langle \Psi_f(N) | a_p^+ | \Psi_c(N-1) \rangle, \tag{40}$$

where

$$\Psi_c(N-1)\rangle = a_c | \Psi_0(N) \rangle \tag{41}$$

has been introduced as a new reference state. We define a Green's function G_{kl}^c for this reference state by replacing $\Psi_0(N)$ by $\Psi_c(N-1)$ in Eqs. (1) and (4).

$$G_{kl}^c(\omega) = -\mathrm{i} \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t} \langle \Psi_c(N-1) | T\{\hat{a}_k(t) \hat{a}_l^+\} | \Psi_c(N-1) \rangle. \tag{42}$$

The electronic factors in Eq. (40) are then by definition the residues of the one-particle Green's function given above, res G_{kl}. Using the one-particle Green's functions the X-ray rates are therefore given as

$$W_f = \sum_{kl} \sum_{i}^{xyz} \langle \phi_l | d_i | \phi_c \rangle \langle \phi_c | d_i | \phi_k \rangle \operatorname{res}_{\omega_f} G_{kl}^c, \tag{43}$$

where ω_f is the pole corresponding to the final state electron affinity of the core ionized system.

Thus under the assumptions given above the Green's function analysis of the X-ray absorption spectrum will be equivalent to the one for the inverse photoelectron (electron attachment) spectrum of the core hole ion, only different MO factors are involved. The classification scheme of Section 2.3 applies to Eq. (43). The absorbed photon's energy is related to the electron affinities EA_f^c of the core ionized system by

$$h\nu_X = IP_c - EA_f^c \tag{44}$$

where IP_c denotes the core ionization potential of the neutral system. The EA_f^c values are by construction obtained as the negative of the corresponding $(N + 1)$ particle poles of the above Green's function G_{kl}^c. Only the bound-state electron affinity poles are considered in the present framework (i.e. positive EA's). We make no assumption about the initial state ionization potentials and obtain the final X-ray energies in Eq. (44) simply by subtracting the binding energies EA_f^c from the experimental core ionization potentials. The above electron affinities are understood as $EA_f^c = E_c(N - 1) - E_f(N)$ where the ground state geometry is assumed for both states involved (vertical transitions). Since each pole corresponds to its residue entering the transition rate, the correlation properties are the same as those for the transition rates, which will be discussed below. It is interesting to observe the similarity in the treatment of X-ray absorption and emission in the present formalism. However, while the binding energies in the emission case evidently are common for different spectra pertaining to different core holes (the full spectrum is obtained from one single Green's function calculation), they may differ in the absorption case for different core hole sites (due to the different choices of the reference state). One thus needs one Green's function calculation for each different core hole site.

Several approaches have been reported for the calculation of NEXAFS spectra of intermediate size within the one-particle approximation. The most commonly used methods are the static-exchange molecular orbital model, and the multiple scattering X_α methods. These methods cover NEXAFS spectra in both discrete and continuum parts, but interpret the NEXAFS features from quite different physical points of views, the molecular orbital, respectively, potential barriers models. Much of the applications of these models have been focussed to the correlation of resonance positions with the molecular structure. For a recent review we refer to Ref. [61]. Explicitly correlated methods have been used for interpreting NEXAFS spectra to a somewhat less extent. Examples are given by state specific methods, such as configuration interaction [62, 63] and multi-configuration SCF [64] methods, or propagator oriented methods, such as the so-called ADC-2 method [65]. Although these methods have made novel interpretations in terms of multi-electron excitations [62, 63], and vibronic couplings [65], they are rather restricted to size of the molecules that can be studied. Larger molecules have mostly been treated by MSX_α and other semiempirical methods [66], and very recently also by the so-called direct atomic orbital techniques [67].

The method advocated above [68] seems to be particularly suited for a treatment of molecules and polymers on a common correlated *ab initio* level. In contrast to other approaches to NEXAFS via the particle-hole propagator [65], our procedure is based on a special one-particle propagator and thus offers a simpler access to the spectra.

For the polymer case the procedure [68] resembles the Koster–Slater type methods for impurities in solids [69, 70]. It is based on *ab initio* calculations with correlation on the bulk as well as on the clusters (with and without perturbation). Whereas it is impractical to explicitly iterate for effects of the local perturbation on self-consistency [71, 72, 73, 74, 75] if one is interested only in the bound states, we obtain a parameter-free (non-tight-binding) description of the emergence of bound states under influence of the perturbation.

In order to calculate the bound states induced in the band gap of polyacetylene by the presence of the defect representing the equivalent core for the C 1s holes, one has to solve the equation

$$\det[1 - \tilde{G}^0(\omega)V(\omega)] = 0, \tag{45}$$

where $\tilde{G}^0$ is the (correlated) one-particle Green's function of the periodic system in the contravariant atomic orbital basis:

$$\tilde{G}^0_{\mu H, \nu J}(\omega) = \frac{1}{2\pi}\sum_l \int_{-\pi}^{\pi} \mathrm{d}k c_{\mu l}(k) c^*_{\mu l}(k) \frac{P_l(k)\mathrm{e}^{\mathrm{i}k(R_H - R_J)}}{\omega - \omega_l(k)}, \tag{46}$$

where μ, ν are atomic orbital and H, J cell indices, and $\omega_l(k)$ and $P_l(k)$ are the quasi-particle bands and the corresponding residues of the one-particle Green's function of the periodic system, and $c_{\mu l}$ are the Hartree–Fock crystal orbital eigenvector coefficients.

The defect matrix of the inverse one-particle Green's function is given by

$$V_{\mu,\nu}(\omega) = \sum_l c^p_{\mu l} c^{p*}_{\nu l} \frac{\omega - \omega^p_l}{P^p_l} - \sum_l c^0_{\mu l} c^{0*}_{\nu l} \frac{\omega - \omega^0_l}{P^0_l}, \tag{47}$$

where $c^0_{\mu l}$ and $c^p_{\mu l}$ are the cluster Hartree–Fock eigenvector coefficients for the unperturbed and the equivalent core system, respectively, ω^0_l and P^0_l are the corresponding poles and residues of the cluster one-particle Green's functions, respectively. The dimension of the above secular problem is determined by the cluster size inherent in the atomic orbital indices of V. It comprised six CH_2 units in a double-zeta basis in the case of polyacetylene [68].

The calculations by this method [68] show that the lowest bands in the discrete butadiene and hexatriene spectra are due to core excitations to the lowest π^* levels pertaining to the different core–hole sites, that the second strong-intensity regions in these spectra are composed of several strong σ excitations, and that there is a significant reduction of the π-to-σ intensity ratio with addition of C_2H_2 units.

Butadiene has been shown as an example for which symmetry selection rules of NEXAFS can be used to correlate spectral features with the orientation of a molecule on a surface [76]. In order to see what information Green's function calculations can supply in this respect, we review the butadiene case in some detail. The low energy part of the butadiene spectrum contains an intensive double-band feature. This feature is well reproduced by the Green's function calculation [68] which places the two C1s-π^* transitions at 285.22 and 284.94 eV for middle and end carbon 1s hole with intensities in a ratio of 2.07:0.97. The calculation thus confirms the interpretation [64] of this double-peak feature as due to chemically shifted transitions to the first π^* level from the end and mid-carbons. Further up in the butadiene spectrum, at 287–289 eV, there is an odd three peak structure, and even higher up one finds broad features ranging between 10 and 30 eV above the ionization threshold, assigned to σ type shape resonances [77]. The interpretation of the 287–289 feature is controversial. MCSCF calculations [64] indicated that σ-type excitations contribute to this feature. Polarization measurements of butadiene on a silver surface [77] did not reveal σ excitations but supported a second π^* level at 288 eV. The polarization dependence of the three higher lying resonances was the reverse, indicating σ resonances (C–H*, $\sigma^*_{\mathrm{C-C}}$, and $\sigma^*_{\mathrm{C=C}}$). It is therefore interesting that the Green's function calculations [68] predict a number of peaks in the region; the two lower and more intensive ones are of σ symmetry the higher one of π symmetry. The large intensity indicates by itself the valence character of these excitations. Thus both the MCSCF and Green's function calculations reject the notion of two single π^* levels at 284 and 288 eV as inferred from a building block principle.

For hexatriene and larger polyenes it is interesting to explore to what extent the "chemical shift" of the C1s-π^* excitation covariance the C1s electron binding energy. The first of the two intense bands in the hexatriene spectrum comprises the three C1s-π^* transitions corresponding to the middle-, penultimate- and end carbons, respectively [68]. It can be noted that the end carbon has the lowest excitation energy and the penultimate carbon the highest. This complies with that the end carbon also has the lowest ionization potential (IP) and the penultimate carbon the highest [57]. Since initial state effects are ignorable for core IPs of hydrocarbons this reflects differences in the core hole screening relaxation between the different carbon atoms.

The one-particle approximation is sufficiently well recovered by the Green's function calculations to warrant an MO analysis. However, the molecular orbitals to be used for interpretation should be the ones corresponding to the final states, relaxed and relocalized according to each particular core hole. The building block picture in which the larger oligomer spectra are derived from overlapping orbitals of the ethylene subunits is not warranted.

For polyacetylene the lowest π transition rate is very small in the uncorrelated calculation. In the correlated calculation the electron affinity of the core ionized system for this transition seems to be merging with the onset of the valence band of the unperturbed system which the calculation places at 5.32 eV binding energy with respect to the core IP (290.2 eV [57]). The effects on the transition rate of this state indicates delocalization of the screening π electrons, in agreement with the finding that the states seem to interact strongly with the bulk plane-wave states. This trend is already indicated by the oligomer results, where the lowest π state transition rates for a middle C1s hole are rapidly decreasing with chain length. A different behaviour than for the π states is displayed by the σ type bound states. For these states the transition rates remain of the same order of magnitude for all chain lengths, which points to less delocalized states. The binding energy with respect to the core IP is 1.60 eV for polyacetylene and thus slightly smaller than for the oligomers (2.49 eV for butadiene and 1.84 eV for hexatriene). The peak at 284.1 eV in the experimental core excitation spectrum of polyacetylene [78] should, therefore, be a π state. The calculations of polyacetylene predict a significant reduction of the $\pi:\sigma$ intensity ratio, which is in line with the reduction of this ratio obtained in the calculations for the oligomer sequence.

3.5 One-photon absorption spectra

The possibility to compute polarization propagators or *response functions* by solving response equations of large dimensions has opened a broad niche of molecular applications. The propagator of Eq. (3) can be expressed as

$$\langle\langle A;B\rangle\rangle^{r}_{\omega_1} = -{}^{e}\boldsymbol{A}^{[1]}({}^{e}\boldsymbol{E}^{[2]} - \omega_1^{e}\boldsymbol{S}^{[1]})^{-1}\boldsymbol{B}^{[1]} \tag{48}$$

and obtained by solving the linear set of equations

$$\boldsymbol{N}^{b}(\omega_1) = ({}^{e}\boldsymbol{E}^{[2]} - \omega_1^{e}\boldsymbol{S}^{[1]})^{-1}\boldsymbol{B}^{[1]}. \tag{49}$$

It can thus simply be expressed as the solution vector times a property vector.

$$\langle\langle A;B\rangle\rangle^{r}_{\omega_1} = -{}^{e}\boldsymbol{A}^{[1]}\boldsymbol{N}^{b}(\omega_1). \tag{50}$$

The ingoing frequencies (ω_1) are obtained by first solving a response eigenvalue equation. The definitions of the constituent matrices, hessian- ($\boldsymbol{E}^{[2]}$), metric- ($\boldsymbol{S}^{[1]}$) and property- ($\boldsymbol{A}^{[1]}, \boldsymbol{B}^{[1]}$) matrices, can be found in the original articles [29, 79]. The large dimensional solutions are obtained by direct iterative techniques, by matrix times trial vector multiplications without storing the generating matrix explicitly, as in optimization of large scale correlated wave functions (direct CI [80], direct MCSCF [81]). Thus the sum-over-state value for the property in question can be obtained without having to perform the summations in Eq. (3) explicitly, or having to diagonalize the hessian or metric matrices completely, something which is prohibited for any but the smallest systems. This methodology is well documented, see e.g. Refs. [29, 79, 82, 83], and many current applications have demonstrated its utility in broad contexts.

In the response or polarization propagator methodology the one-photon spectrum, viz. excitation energies and transition moments, are obtained from the single and double residues for the linear response function. The shorter polyenes serve as good test cases for such calculations since undisputable experimental results are available for comparison. The one-photon spectra and the optical properties of polyenes are important also because they have a bearing on the possible conducting properties of the corresponding polymer. Thus the simulations of polarons and solitons in longer doped chains should preferably be carried out with methods that can address the one-photon spectra properly. The distribution of oscillator stengths, the organization of the lowest excited states, and in particular the band gap must be reproduced correctly. The electronic one- and two-photon spectra become progressively more compressed with a narrowing band gap with the length of the chain, and excitation energies and oscillator strengths must be reliable in order to assign spectra. With this in mind one- and two-photon absorption spectra (OPA and TPA) of ethylene , trans-butadiene, trans-hexatriene and trans-octatetraene were recently investigated by means of linear and quadratic response theory calculations in Ref. [84]. It was demonstrated that accurate results for the one-photon excitation spectra of these short polyenes indeed can be obtained already at the lowest level of response theory, namely the random phase approximation (time-dependent Hartree–Fock). The excellent agreement with experiment, within one or two tenths of an eV for all four molecules, indicated that the comparatively simple but still well-defined random phase approximation (RPA) method has important ramifications for the study of linear optical properties of the conjugated polyenes. It is relevant to mention that polarizabilities generated by RPA are within a few percentage of the vapour phase values at the corresponding frequencies. Accurate polarizabilities are prerequisites for calculations of the one-photon spectra since they connect through the second order sum rule for spectral moments. In response theory gauge invariance and sum rules are obtained in the limit of a complete basis set, which also are useful facts for qualifying obtained results.

The excited states of the polyene molecules can be divided into two categories according to the selection rules imposed by symmetry. The first kind of states are one-photon allowed only, while the second kind only can be reached by two-photon transitions. The energetics of one-photon transitions have been carried out by different theoretical methods, and by RPA as early as 1971 (spectrum of ethylene molecule computed by Shibuya and McKoy [85]). Excited state energies of ethylene has also been studied with the random phase approximation by Bouman and Hansen 1985 obtaining quite good agreement with experimental data [86]. More recently spectra have been obtained using multi-configuration linear response [79] (MCLR), however, most of the success of later applications must still be ascribed the use of good basis sets, giving results believed to be close to the RPA basis set limit for one-photon spectra and polarizabilities [84]. Basis sets of two categories have mostly been applied, namely polarizability consistent [87, 88] and correlation consistent [89] basis sets optimized for the constituent atoms, and augmented with sets of appropriate diffuse functions [90].

Concerning the detailed assignments of the polyene spectra one has mostly focussed on the lowest one-photon allowed ^1B_u states and the lowest one-photon forbidden ^1A_g states (discussed in next section). The excitation energy for the 1^1B_u state of butadiene, which represents the major feature in its electronic spectrum, has been a key issue in a large number of theoretical studies. The results have, however, been rather disparate [4], something that is claimed to derive from the delicate balancing of Rydberg and valence contibutions to this state. Only two very recent computations have given excitation energies for this state in reasonable agreement with the experiment, 6.14 eV [91] and 6.12 eV [90], compared to the experimental value of 5.92 eV. From this outset, the excellent agreement obtained by RPA is quite remarkable, within few hundreds of an eV for different basis sets [84]. That this is not fortuitous can be understood by that similar calculations give excitation energies for ten singlet states with an error less than 0.19 eV compared with available experimental data. Also oscillator strengths obtained at the RPA level are found close the experimental values when these are available. The general experience from aromatic compounds for which experimental oscillator strengths occasionally are available, is that they indeed are well recapitulated by linear response theory [92], although in that case excitation energies from RPA are of somewhat poorer quality than for the aliphatic compounds. With excitation energies and oscillator strengths of good quality, successful assignments of spectra as complicated as that of hexatriene and octatetraene can be accomplished [84]. Going to larger polyenes reliable oscillator strengths are absolutely crucial in order to sustain assignments.

It is ironic to note that the lowest level of response theory, RPA, gives one-photon excitation energies of the short polyenes of the same quality, or actually even better than the most sophisticated state-specific methods (n.b. CASPT2 [90]). This is certainly not the case for the aromatic compounds [93]. The excellent agreement found for polyenes and other aliphatic compounds [84] have important consequences, since RPA is both well-defined, size extensive and applicable to large species. This has recently been demonstrated through the development of so-called direct atomic orbital techniques for both linear and quadratic RPA [94, 5]. MCLR with limited correlation spaces, e.g. π spaces, does not necessarily improve results, since the static (valence) and dynamic (non-valence) electron correlation in general tend to have opposite effects for hydrocarbons like the polyenes. It has also been found that state-specific CASSCF calculations even give a reversed order for the ^1B_u states with the valence state above the Rydberg states [90]. Calculations performed with Hamiltonian including π-electrons also exclude dynamic correlation, and results obtained from methods like PPP or extended Hubbard can be of mixed quality.

The success of RPA for polyenes is somewhat hard to rationalize since response theory calculations cannot be compared directly with state specific methods with respect to correlation. RPA is generally considered appropriate for states described by wave functions with dominating single excitations; it is a single-particle–hole approximation to excited states which allows for the presence of two-particle and two-hole pairs in the ground state [85, 95]. Its multi-configurational analogue [79]

(MCLR) "adds correlation" to the excited states more than that covered by the ground state correlating space. In any case, providing a set of excitation energies and oscillator strengths in one batch of calculations, linear response theory is a very powerful tool for assigning complex one-photon spectra such as those of the short polyenes.

3.6 Two-photon absorption spectra

The generalization of polarization propagator theory to non-linear phenomena has made possible many new interesting applications with respect to modern spectroscopy. As for the linear case the computation of quadratic response functions alleviate previous obstacles for systems described by large-dimensional wave functions, in principle by solving sets of equations rather than by performing explicit summations. Applications have been carried out for different phenomena such as two-photon absorption, hyperpolarizabilities and phosphorescence. The derivations of linear and quadratic response functions and their residues can be found in the original paper on quadratic response theory applied to exact and MCSCF states by Olsen and Jørgensen in Ref. [29]. Briefly stated, the evaluation of the quadratic response function for operators A, B and C (here components of the dipole operator) is expressed as [29] (Einstein summation)

$$\begin{aligned}\langle\langle A;B,C\rangle\rangle_{\omega_1,\omega_2} = {} & N^a_j(\omega_1+\omega_2)B^{[2]}_{jl}N^e_l(\omega_2) + N^a_j(\omega_1+\omega_2)C^{[2]}_{jl}N^b_l(\omega_1) \\ & + N^b_j(\omega_1)(A^{[2]}_{jk} + A^{[2]}_{kj})N^c_k(\omega_2) \\ & - N^a_j(\omega_1+\omega_2)(E^{[3]}_{jlm} + E^{[3]}_{jml} - \omega_1 S^{[3]}_{jlm} \\ & - \omega_2 S^{[3]}_{jml})N^b_l(\omega_1)N^c_m(\omega_2) \end{aligned} \tag{51}$$

where $\boldsymbol{E}^{[3]}$ and $\boldsymbol{S}^{[3]}$ in Eq. (51) are generalizations of the RPA Hessian and metric matrices, while $\boldsymbol{A}^{[2]}$ $(\boldsymbol{B}^{[2]}, \boldsymbol{C}^{[2]})$ are generalizations of the property matrix $\boldsymbol{A}^{[1]}(\boldsymbol{B}^{[1]}, \boldsymbol{C}^{[1]})$ and are given in Ref. [29]. In order to obtain the ingoing solution vectors $\boldsymbol{N}^a$, $\boldsymbol{N}^b$ and $\boldsymbol{N}^c$ one needs to solve the three linear sets of equations

$$\begin{aligned} \boldsymbol{N}^a(\omega_1+\omega_2) &= [(\boldsymbol{E}^{[2]} - (\omega_1+\omega_2)\boldsymbol{S}^{[2]})^{-1}\boldsymbol{A}^{[1]^+}]^+, \\ \boldsymbol{N}^b(\omega_1) &= (\boldsymbol{E}^{[2]} - \omega_1\boldsymbol{S}^{[2]})^{-1}\boldsymbol{B}^{[1]}, \\ \boldsymbol{N}^c(\omega_2) &= (\boldsymbol{E}^{[2]} - \omega_2\boldsymbol{S}^{[2]})^{-1}\boldsymbol{C}^{[1]}. \end{aligned} \tag{52}$$

The single residue of the quadratic response functions gives the second-order transition moment between the reference state $|0\rangle$ and the final state $|f\rangle$. It may be expressed in terms of the two solution vectors $\boldsymbol{N}^a(\omega_f - \omega_1)$ and $\boldsymbol{N}^b(\omega_1)$ and the eigenvector $\boldsymbol{X}_f$ $(\boldsymbol{E}^{[2]} - \omega_1\boldsymbol{S}^{[2]})X_f = 0)$.

$$\begin{aligned} - & \left\{\frac{\langle 0|A|j\rangle\langle j|(B - \langle 0|B|0\rangle)|f\rangle}{(\omega_j - \omega_f + \omega_1)} + \frac{\langle 0|B|j\rangle\langle j|(A - \langle 0|A|0\rangle)|f\rangle}{(\omega_j - \omega_1)}\right\} \\ & = -N^a_j(\omega_f - \omega_1)B^{[2]}_{jl}X_{1f} - N^b_j(-\omega_1)(A^{[2]}_{jl} + A^{[2]}_{lj})X_{lf} \\ & + N^a_j(\omega_f - \omega_1)(E^{[3]}_{jml} + E^{[3]}_{jlm} - \omega_1 S^{[3]}_{jml} - \omega_f S^{[3]}_{jlm})N^b_m(-\omega_1)X_{lf}, \end{aligned} \tag{53}$$

If operators A, B, and C refer to components of the dipole operator, the quadratic response function in Eq. (51) gives the first hyperpolarizability. Its single residue gives the two-photon transition matrix element, and its double residues the transition matrix elements between the excited states $\langle g|$and$|f\rangle$. Two-photon absorption spectra have been obtained with this formalism in several computational studies, for small molecules [96], for aromatic [97, 98] and aliphatic [84] compounds. These studies include also the role of vibronic contributions to the induced two-photon spectrum, which in general are found to be quite important.

As shown in Section 3.5 one-photon spectra and other linear properties of polyenes have been well characterized through propagator calculations. Much of the theoretical efforts focus now on non-linear properties of these systems. The non-linear optical responses, the mechanism of the optical linearity and non-linearity, the length dependence of hyperpolarizabilities and multi-photon spectra in oligomer sequences have constituted few of several items of interest. For polyenes, the two-photon absorption of even states and their positions with respect to the band gap is of particular interest, since it is the key point for understanding optical non-linearity of polyacetylene.

Two-photon spectra of the short polyenes were investigated by the quadratic RPA method in Ref. [84]. Two-photon absorption maxima for the even states of transbutadiene, trans-hexatriene and trans-ocatetraene were located at 1.5–1.7 times the band gap energy (E_g). The first one-photon forbidden ^1A_g state was found to have a very small two-photon amplitude, and is therefore likely not to contribute significantly to the non-linear properties of the polyenes, although it might intrude the one-photon band-gap. The mechanism of optical non-linearity in the short conjugated polyenes was explored in relation to the so-called three- and four-state models.

As mentioned in the previous paragraph much of the interest in the optical properties of the polyenes focus on the location of the one-photon allowed, $1\,^1B_u$ state, and on the dipole forbidden, but two-photon allowed, $2\,^1A_g$ state. The odd states (^1B_u) and even states (^1A_g) are antisymmetric and symmetric with respect to the mirror plane passing through the center of the chain, respectively. The $1\,^1B_u$ state is thought to define the band gap at least for the shorter polyene members, however, whether this is the case for the longer ones is still an open question because the assessment of the $2\,^1A_g$ state has been somewhat ambiguous both from experimental and theoretical points of view. It is thus still uncertain for which compounds this state intrude into the band gap. For example multiphoton experiments [99, 100] assign the first ^1A_g peak in gas-phase hexatriene to 6.2 eV while two-photon experiments on liquid phase hextriene assigns it to 5.2 eV. The position of the $2\,^1A_g$ state has been shown sensitive to solvent effects, to geometrical distortion and bond-order inversion. For many polyenes the out-of-plane deformation of the S_1 state increases its nonradiative internal conversion dramatically [101].

The indication now is that for longer polyenes the $2\,^1A_g$ state is the lowest excited state, and octatetraene seems to constitute an inflexion point in this context. Very recent studies on gas-phase trans-trans octatetraene favour a low $2\,^1A_g$ state assignment; fluorescence spectroscopy [102], experiments using free jet expansions [103], as well as large scale the multi-configurational perturbation theory calculations [104]. RPA response theory calculations give very good experimental agreement for the ^1B_u state but fails to find a ^1A_g state below $1\,^1B_u$ state for octatetraene. Beside this state, results agree with state-specific calculations [104] (CASPT2) on the excitation energies of the ^1A_g states, and give a two-photon peak maximum around 8 eV. The role of geometric relaxation [105] will also have a bearing on the location on the first excited ^1A_g state. As in the case for some ring systems [98] the RPA two-photon amplitude for the first excited ^1A_g state is quite small and therefore not important for the non-linear behaviour of polyenes as previously expected, while the higher lying ^1A_g states with large two-photon intensity are more important. Calculations on hyperpolarizabilities illuminate this point [84].

The common features of two-photon transitions in the polyenes are also discussed in Ref. [84] based on response theory results. Calculations of the two-photon absorption (TPA) intensity, δ_t, assuming two linearly polarized light beams with parallel polarization vectors were carried out. This intensity is expressed as [97, 98])

$$\delta_t = (S_{xx} + S_{yy} + S_{zz})^2 + 2(S_{xx}^2 + S_{yy}^2 + S_{zz}^2 + 2S_{xy}^2), \tag{54}$$

where S_{ij} denotes single residues of the quadratic response functions for dipole operators i and j. Results indicate a quite strong basis set dependency, however, some common features for all the short polyenes could anyway be extracted. The number of states is not the same for the different basis sets, while the positions of the maxima stayed very close.

The TPA maximum for the butadiene (BD) molecule is obtained at about 1.5 E_g, where E_g is the excitation energy of the first odd state (1^1B_u), i.e. the optical gap. A diffuse structure near 7.4 eV for hexatriene (HT) assigned as a $^1A_g \leftarrow {}^1A_g$ transition [106, 107], and a relatively strong TPA at 6.24 eV appearing in gas phase multiphoton spectra of BD [100], are confirmed by the RPA calculations. The TPA maximum is located around 8.1 eV or 1.6E_g for HT, while for the octatetraene (OT) molecule it is located at 7.82 eV or approximately at 1.7 E_g. Thus the BD, HT and OT molecules show, irrespective of basis sets, the common feature of a band maximum around 1.5–1.7 E_g. From the RPA calculations [84] a second strong TPA located around 1.2–1.4 E_g could be derived for the BD, HT and OT molecules.

The two-photon spectra, the transition moments between excited states and the hyperpolarizabilities are all interconnected, and can all be derived from the response functions. Thus the transition moments between excited states can be used to construct few-state models for the hyperpolarizability. These models have been used semi-empirically to investigate the mechanisms behind optical non-linearity [108–110] in conjugated polymers. *Ab initio* methods have so far only attempted to reproduce experimental hyperpolarizabilities [111–113], e.g. using coupled Hartree–Fock theory (equivalent to RPA). Karna et al. computed the frequency-dependent hyperpolarizabilities of the short polyenes [112, 111, 84]. In general it is found that the basis set and dispersion effects play the dominant roles in determining the hyperpolarizabilities of polyenes, while correlation effects might be rather small [111]. From response theory methods and decomposition schemes it is thus also possible to explore the mechanism of non-linearity at a purely *ab initio* level, see Ref. [84].

From the sum-over-states expression for the response function (see Ref. [29]), it is fairly straightforward to derive the three- and four-state model expressions for the static hyperpolarizability [84]. These expressions involve transition moments and the energy difference between the few low-lying states. In polyenes the hyperpolarizability is dominated by the xxxx component along the chain, which is controlled by the transition route $1\,^1A_g \rightarrow a^1B_u \rightarrow b\,^1A_g \rightarrow c\,^1B_u \rightarrow 1\,^1A_g$ where a, b and c denote state numbers. For instance, in the three-state approximation, only the $1\,^1A_g$, $1\,^1B_u$ and $m\,^1A_g$ states are considered [108]. When the transition moment between the odd ($1B_u$) state and the excited even state (mA_g) is larger than that between the ground state and the odd ($1B_u$) state, the hyperpolarizability is positive, otherwise it is negative. Response theory calculations presented in Ref. [84] indicate, however, that some of these conditions for the three and four-state models are not well fulfilled for polyenes, and that many transitions must be accounted for to explain the large positive value for the xxxx component. Thus, although there is an even state which dominates the TPA spectrum, it cannot be used as a candidate to form three- or four-state approximations for determining the hyperpolarizability. This finding is in contrast to for instance charge transfer complexes [114], for which few state models represent the hyperpolarizability very well.

3.7 Singlet–triplet spectra

The role of triplet states in electronic spectroscopies has been little investigated in comparison with the role of the manifold of singlet states. This follows from the simple fact that transitions to many of the lowest singlet states are dipole allowed and therefore well characterized by absorption or fluorescence spectroscopy, and, on the theoretical side, from the comparatively simple handling of the dipole interaction for singlet states. This should be weighted against the non-linear nature of the interaction, with simultaneous spin–orbit and dipole coupling, that is involved in the absorption or emission of triplet states.

From the generalization of linear and quadratic response theory to include triplet operators, and in particular the spin–orbit operator [115–117], it is now possible to characterize a whole range of properties of triplet states. The spin–orbit operator enters as one of the perturbing operators in quadratic response theory to describe singlet–triplet absorption or phosphorescence. The prospect for spin–orbit response and, in general, for excitations involving change of spin was greatly promoted by the formulation of determinant based CI techniques [115, 118]. This simplified the construction of two-electron density matrices that contain triplet orbital excitation operators and two-electron density matrices which connect singlet and triplet states.

In addition to one-photon singlet–triplet absorption spectra the interest has focussed on the phosphorescence effect, which has been analysed by response theory for a series of small molecules as well as for several aromatic compounds [93, 119, 120]. The information gained from such calculations concern polarization directions, vibronic activity, oscillator strengths, radiative lifetimes and excitation energies. These quantities either refer to values averaged over the triplet states or to the specific triplet state spin sublevels. Modern low-temperature matrix isolation techniques allow comparison with experimentally determined spin-sublevel lifetimes. At very low temperatures the spin lattice relaxation processes are slower than the phosphorescence decay time which means that characterization of the individual spin sublevels can be performed in terms of decay constants and polarization directions.

The phosphorescence lifetime is determined from the rate of the spin-forbidden dipole transition between two electronic states of different multiplicity. For a system with a singlet ground state S_0 and a first excited triplet state T_1, the lifetime associated with the kth triplet component T_1^k is (in atomic units)

$$\frac{1}{\tau_k} = \frac{4\omega_1^3\alpha^3}{3}\sum_l |\langle S_0|x^l|T_1^k\rangle|^2 \tag{55}$$

where $\omega_1 = E(T_1) - E(S_0)$ is the frequency of the transition, α is the fine-structure constant and x^l is the lth component of the dipole operator. The total radiative lifetime (in the high-temperature limit) τ is obtained as $3/\tau = \sum_k 1/\tau_k$. The transition matrix element is determined from first-order perturbation theory as

$$\langle S_0|x^l|T_1^k\rangle = \sum_s \frac{\langle S_0|x^l|S_s\rangle\langle S_s|H_{SO}^k|T_1^k\rangle}{E(T_1)-E(S_s)} + \sum_t \frac{\langle S_0|H_{SO}^k|T_t^k\rangle\langle T_t^k|x^l|T_1^k\rangle}{E(S_0)-E(T_t)} \tag{56}$$

where H_{SO}^k is the kth component of the spin–orbit operator. In the language of propagators or *response functions* this matrix element is associated with the residue of a quadratic response function;

$$\begin{aligned}\lim_{\omega\to\omega_1} (\omega-\omega_1)\langle\langle x^l; H_{SO}^k, C\rangle\rangle_{0,\omega} = {} & -N_j^r(\omega_f)H_{SO_{jl}}^{[2]}X_{lf} \\ & - N_j^{SO}(r_{jl}^{[2]} + r_{lj}^{[2]})X_{lf} + N_j^r(\omega_f)(E_{jml}^{[3]} + E_{jlm}^{[3]} - \omega_f S_{jlm}^{[3]})N_m^{SO}X_{lf},\end{aligned} \tag{57}$$

where C is an arbitrary triplet operator and an Einstein summation convention is used. This equation is similar to the one given for two-photon transitions in the previous section; the phosphorescence case involves dipole and spin–orbit linear response vectors $\boldsymbol{N}^r(\omega_f)$ and $\boldsymbol{N}^{SO}$ that are obtained by solving the two linear response equations

$$\boldsymbol{N}^r(\omega_f) = (\boldsymbol{E}^{[2]} - \omega_f \boldsymbol{S}^{[2]^{-1}} \boldsymbol{r}^{[1]^\dagger}]^\dagger, \tag{58}$$

$$\boldsymbol{N}^{SO} = (\boldsymbol{E}^{[2]})^{-1}\boldsymbol{H}_{SO}^{[1]} \tag{59}$$

and the triplet excitation vectors (X_f) and frequencies (ω_f) are obtained from the solution of the MCSCF triplet excitation eigenvalue equation. Thus, with response theory the singlet–triplet transition matrix element is acquired directly from the residues of response functions, by iterative solutions of the response equations of large dimensions.

Polyenes lack in general observable emission from their triplet T_1 states. Being of $\pi\to\pi^*$ nature there is no strong spin–orbit coupling to the dipole intensive singlet $\pi\to\pi^*$ states through which an observable phophorescence can occur. The T_1 state receives most intensity through interaction with the dipole-weak and high-lying $\sigma\to\pi^*$ states. Calculations of singlet–triplet absorption and triplet state phosphorescence spectra of the short polyenes were recently carried out in Ref. [105]. Because triplet response calculations can be subject to instabilities at the RPA level (with a Hartree–Fock reference state), as it indeed is for ethylene, singlet-triplet response calculations are mostly carried out with correlated (multi-configurational-) reference states. In contrast to the common case of fluorescence, involving singlets which are comparatively short-lived and therefore well characterized by calculations assuming the vertical approximation, the long-lived triplet states often require calculations at both the vertical and the adiabatic points. Geometry optimizations of the T_1 states should be performed, since this will be important not only for the electronic radiative lifetime, but also for the vibronic contributions and the role of alternative (non-radiative) decay channels to the triplet state.

As in the case of the polyene singlet spectra, the first B_u state of butadiene seems to have been a key issue in theoretical studies of polyenes considering also the manifold of triplet states. It has previously been claimed [121] that the lack of experimental observation of the ${}^1A_g$–${}^3B_u$ transition is due to the presence of a lower

^3A_g state with forbidden phosphorescence but which quenches the dipole intensity from the ^3B_u state. However, calculations in Ref. [105] clearly show that at optimum geometry the ^3B_u state is the lowest triplet state and that the lack of observation simply is due to very weak phosphorescence. The radiative lifetime was predicted to 24*s* for the singlet optimized geometry and as long as 327*s* for the triplet optimized geometry. The response results for the other short polyenes are also of this magnitude, which might explain the lack of observation. However, the geometric distortions, all T_1 states are found eclipsed and pyramidalized, and the vibronic contributions are important factors that must be accounted for in addition to the non-radiative quenching of this emission.

Linear spin–orbit response theory [116] can also be used to explore the probabilities of non-adiabatic singlet–triplet transitions, the so-called intersystem crossings. Such calculations were carried out in Ref. [105] for the polyene series. As pointed out by Mulliken [122] already 60 years ago, acyclic alkenes, unless extensively conjugated, are expected to show energy maxima in the ground singlet state and minima in the first excited triplet state at a perpendicularly twisted geometry. Thus ethylene in the T_1 state is expected to belong to the D_{2d} group. Since at this geometry the energy gap between the S_0 and T_1 states is quite narrow it has generally been assumed that it represents the geometry at which T_1–S_0 nonradiative transition or intersystem crossing (ISC) occurs [123, 124]. In spite of the small energy gap the rate of $S_0 \rightarrow T_1$ ISC could be inefficient, because the spin–orbit coupling (SOC) matrix element between the two states is equal to zero at the D_{2d} symmetry. In Ref. [105] geometry optimization of the ethylene T_1 state was performed showing that the two CH_2 groups are pyramidalized up to the angle 9°. At this angle the SOC matrix element is equal to 0.03 cm^{-1} and therefore still too small. It was suggested that the S–T crossing could occur in the region of $\gamma \simeq 85°$, where γ is a twist dihedral angle between the HCH planes; at this geometry the SOC matrix element is of the order of 0.2 cm^{-1} [124]. This is sufficient for the effective quenching of the T_1 state (the crossing point is passed many times during vibrations of the twisted T_1 ethylene), but too small for the $S_0 \rightarrow T_1$ ISC transition during thermal isomerization.

4. Concluding remarks

In the present work we have discussed various molecular electron spectroscopies under the unifying aspects of contemporary propagator theory. The finite polyenes and polyacetylene have been employed as common test samples for this purpose. The usefulness of the propagator methods is obvious from their applications which now cover a representative cross section of chemically and physically interesting problems. Although the diversification of these methods already has been driven quite far, one can forsee development in several aspects; of the basic methodology as well as of a widening of the scope of systems and phenomena that can be investigated. It is our hope that the present review has provided ideas on some propagator oriented problems that will be worked on in the field of molecular electron spectroscopy.

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