Time-Dependent Local-Density Approximation in Real Time: Application to Conjugated Molecules

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ABSTRACT: The time-dependent local-density approximation (TDLDA) is applied to the optical response of conjugated carbon molecules in the energy range of 0–30 eV, with calculations given for carbon chains, polyenes, retinal, benzene, and C₆₀. The major feature of the spectra, the collective π – π * transition, is seen at energies ranging from below 2 to 7 eV and is reproduced by the theory to a few tenths of an electron volt with a good account of systematic trends. However, there is some indication that TDLDA predicts too much fragmentation of the strength function in large molecules. Transition strengths are reproduced with a typical accuracy of 20%. The theory also predicts a broad absorption peak in the range of 15–25 eV, and this feature agrees with experiment in the one case where quantitative data is available (benzene). © 1999 John Wiley & Sons, Inc. Int J Quant Chem 75: 55–66, 1999

Key words: optical absorption; time-dependent density functional theory; conjugated carbon molecules; polyenes

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Introduction

ean-field theory is widely used in chemistry and physics, giving an approximation that is very robust in its domain of validity. Particularly successful is the density functional theory [1], which treats the electron-electron interaction in a local-density approximation (LDA), i.e., by adding a density-dependent contact term to the Hartree Hamiltonian. The theory is commonly used to calculate ground-state structures of molecules and condensed systems. A corresponding theory for excitations is the time-dependent local-density approximation (TDLDA), which has also been applied to a number of systems [2-13]. In these works, the TDLDA equations were solved with various methods starting from an energy representation. The equations can also be solved directly in real time, and for some purposes that approach is more efficient. It allows one to calculate the effects of strong fields without complicated perturbative expansions. In the small-amplitude linear response regime it gives the entire response associated with the sum rule in one calculation. In this work we wish to demonstrate the utility of the real-time approach using as example the electromagnetic response of conjugated carbon molecules. As a second purpose, we wish to investigate the domain of validity of a simple adiabatic energy-density functional by comparing its predictions to the measured properties and the results of other methods.

Our calculation will be ab initio from the point of view of the electrons, since we take the electron Hamiltonian from well-known prescriptions used in ab initio density functional theory. However, we will not attempt to use the Hamiltonian to arrive at the nuclear coordinates; the ground-state problem has been well studied by others, and our interest here is in the excitations. In the next section we describe our numerical implementation of the TDLDA and make some qualitative comparisons with other methods. Then we apply the method to polyenes, retinal, benzene, and C₆₀.

Theory

FORMAL ASPECTS

The TDLDA theory is closely related to the time-dependent Hartree-Fock equation intro-

duced by Dirac [14]. That theory can be derived from a variational principle,

$$\delta \int dt \langle \Psi | H - i\hbar \frac{\partial}{\partial t} | \Psi \rangle = 0.$$
 (1)

Here Ψ is restricted to be a Slater determinant of single-electron wave functions ϕ_i , $\Psi = \mathscr{A}\prod_i \phi_i$. The corresponding static variational principle is the usual energy minimization principle from which one derives the Hartree–Fock equations. The LDA theory is obtained in the same way, using the LDA energy functional instead of $\langle \Psi | H | \Psi \rangle$ in Eq. (1). The derived TDLDA equations of motion are given by

$$-\frac{\hbar^2 \nabla^2}{2m} \phi_i + V_{\rm ion} \phi_i + e^2 \int dr' \frac{n(r')}{|r-r|} \phi_i + V_{\rm xc}[n(r)] \phi_i = i\hbar \frac{\partial}{\partial t} \phi_i, \quad (2)$$

where $n(r) = \sum_i |\phi_i(r)|^2$ is the electron density. The $V_{\rm xc}$ is the exchange–correlation potential, related to the exchange-correlation energy $v_{\rm xc}$ by $V_{\rm ex} = dv_{\rm xc}/dn$.

Several general remarks can be made here. Practitioners of the density functional theory often claim justification for the Kohn-Sham equations based on formal existence theorems. Theorems can also be proven for the time-dependent case [15], but our own partiality to the theory is based on more pragmatic considerations. First, if the time dependence is slow, the TDLDA should be as good as the static theory because the motion would be adiabatic and governed by the same Hamiltonian. Second, integrals of the response over frequency obey sum rules, and these are satisfied in principle by the small-amplitude TDLDA. Since the sum rules are most sensitive to the highfrequency behavior, we see that the TDLDA is good at both extremes, and therefore promising for describing the middle ground.

The next remark concerns the domain of applicability of the theory. The TDLDA describes the system by a single Slater determinant, which can be expressed in a particle–hole basis as a particle–hole operator on the ground state. The theory thus does not contain the degrees of freedom necessary to describe excitation that have a more complex character than single-electron excitations. Not only will the experimental spectrum be more complex due to mixing of states of different particle–hole character, but the coupling to vibrations will broaden the transitions on an energy resolution scale of a few tenths of an electron volt. However, even though the TDLDA only includes single-electron degrees of freedom, it is far superior to the static single-electron theory because it includes dynamic screening effects. The dynamic screening arises directly from the time dependence of the mean-field potential. It shifts transition strength up out of the lowest particle-hole excitations into a higher frequency range, of course preserving the sum rule. This can be a very large effect; in the case of C_{60} considered below the strength of the lowest excitations are reduced by an order of magnitude. In general, what we expect from the TDLDA is the frequency location and strengths of the strong transitions, but not details of its fragmentation into the eigenstates of the many-electron Hamiltonian.

There are several implementations of the TDLDA in the small-amplitude limit, each with its advantages and disadvantages. But we should emphasize that they should in principle be equivalent with the results depending only on the assumed energy density functional. The main techniques using the energy representation are the response function method [9–11] and the matrix Random Phase Approximation (RPA) method [2, 3, 6]. The real-time method has been applied in nuclear physics to describe the small amplitude response [16, 17]. It has also been used to describe the strong-field response of atoms [18] and clusters [19].

The matrix RPA is the only one of these methods that can treat nonlocal interactions such as the Fock term. However, the matrix RPA method uses a particle-hole representation of the perturbed wave function, which becomes inefficient for systems having a large number of particles. The necessity for truncation with large systems can be seen with a simple argument. The number of states in a particle-hole representation is given by the product of the number of particle and hole orbitals, thus scaling as N^2 , where N is the number of electrons. The RPA matrix is thus an $N^2 \times N^2$ matrix, requiring of the order of N^6 operations to diagonalize. Efficiency is obtained by restricting the number of states so that the dimensionality grows only as $N \times N$, and asking only for solutions for specific normal modes or frequency domain. The response function method treats the polarizability of the system as the basic object of study; the dimensionality in representing this function of position scales as N for large systems.

Thus this method does not need any preliminary truncation to reduce the matrix size. The matrix inversion requires a similar numerical effort to the diagonalization, and again efficiency is only possible for considering one energy at a time. In the real-time method, the numerical object of computation is the set of N wave function vectors, each of dimensionality *D* that is proportional to the size of the basis and thus $D \sim N$. The time evolution is carried out by applying the Hamiltonian operator to the wave functions. Here we rely on a representation in which the Hamiltonian is sparse, so that the number of operations for each time step scales as N^2 . The number of time steps required for a given energy resolution is independent of N, so the overall scaling is N^2 .

For our energy density function, we use the widely applied exchange–correlation energy given by Refs. [22, 23]. One can introduce more complicated energy function that have gradient corrections or self-interaction corrections, but it was not clear that there would be an advantage in using a more complicated form.

In addition, we replace the ionic potential by a pseudopotential to eliminate the core electrons from the theory. We use a standard prescription for constructing the pseudopotentials of the ions [24]. This procedure gives a pseudopotential that is nonlocal, depending on the orbital angular momentum of the electron. This has consequences for the sum rules [25], but we believe these are well under control [26]. Numerically, we implement the nonlocality using a separable approximation as described by Ref. [27].

To calculate the electromagnetic response using Eq. (2), we begin with the wave functions for the occupied ground-state orbitals $\phi_i^{(0)}$ as given by the static Kohn–Sham equations. The wave function are then perturbed by multiplying them by a phase factor,

$$\phi_i(0) = e^{ikx} \phi_i^{(0)}.$$
 (3)

Physically, this gives the effect of a short-duration electric field acting on the electrons. The wave functions are then evolved by the time-dependent equation of motion, Eq. (2). Physical observables are extracted from the time-dependent wave function by Fourier transformation. A basic quantity to describe the molecule's interactions is the dynamic polarizability $\alpha(\omega)$. This is essentially equal to the Fourier transform of the time-dependent dipole

moment, namely

$$\alpha(\omega) = \frac{e^2}{k\hbar} \int dt \, e^{-i\omega t} \sum_i \langle \phi_i(t) | \, x | \phi_i(t) \rangle. \quad (4)$$

Another useful quantity is the strength function $S(\omega)$, whose integral is the total oscillator strength. This is defined

$$S(\omega) = \frac{2m\omega}{\pi\hbar^2 k} \int dt \sin \omega t \sum_i \langle \phi_i(t) | x | \phi_i(t) \rangle.$$
 (5)

We shall use the symbol n_e (effective number of electrons) for integral of *S* when we consider the excitation with a specific orientation of the electric field with respect to the molecule. The usual oscillator strength *f* is the same quantity averaged over molecular orientations. The sum rule $\int d\omega S(\omega) = n_e$ may be derived from the short-time behavior of the wave function. The electrons initially respond to a perturbation as free particles, and the dipole moment associated with the perturbation (3) initially evolves as

$$\sum_{i} \langle \phi_i(t) | x | \phi_i(t) \rangle = \frac{n_e k}{m} t + O(t^3)$$
 (6)

NUMERICAL ASPECTS

The numerical algorithm for integrating the time-dependent equations is specified by the choice of basis and the integration technique. We represent the electron wave function on a uniform spatial mesh as done in Refs. [7, 20]. The integration algorithm is identical to one used to solve the TDLDA equations in nuclear physics [21]. An important advantage of spatial meshes is that the single-electron Hamiltonian is a sparse matrix. This allows one to consider vectors for the particle wave function with many tens of thousands of points. Of course, a uniform spatial mesh has the disadvantage that the mesh size is determined by requirements of small regions next to the ion centers. This is alleviated somewhat by the use of pseudopotentials (see below). The important numerical parameters associated with the spatial mesh are the mesh spacing Δx and the total number of mesh points M. Thus the molecules are calculated in a volume $V \sim M(\Delta x)^3$. We represent the Laplacian operator by a higher-order difference operator in our algorithm, as was done in Refs. [20, 21]. For most of our calculations, the surface is treated by taking the wave function to be zero

outside the volume. The required mesh spacing depends on the atomic number of the atom and the pseudopotential used. We require that the equations on the mesh give the converge Kohn–Sham eigenvalues to within 0.1 eV. This is achieved on carbon–hydrogen systems with $\Delta x = 0.3$ Å. The geometry of the volume represented by the mesh is determined by requiring the edge to be at least 4 Å from any ionic center. The number of points needed ranges from 19000 in C₂H₄ to 103000 in C₂₈H₃₀.

The numerical integration requires as a parameter the time step ΔT over which the single-particle Hamiltonian is treated as static. Within the time step the equations are solved by a predictor-corrector method as described in Ref. [21]. The required size of the time step depends on the energy scale of the Hamiltonian. Thus one expects a dependence $\Delta T \sim (\Delta x)^2$. As a practical criterion, we determine ΔT by requiring the norm of the wave function to be accurately conserved. When that is the case, the energy is also conserved to good accuracy. We found that $\Delta T = 0.001 \ \hbar/eV$ is needed for carbon structures with a mesh size of $\Delta x = 0.3$ Å.

Another numerical parameter is the length of the time integration T. The effective resolution of the strength function is determined by this quantity. In the timing tests we show below, the integration time is $T = 10 \hbar/eV$, corresponding to a resolution of $\hbar/T = 0.1$ eV. In the graphs of the strength functions shown later, we have integrated to $T = 30-40 \ \hbar/eV$, giving peaks having widths of less than 0.1 eV. Since the accuracy of the TDLDA does not approach this value, there is no benefit to integrate to longer times. In physical terms, other degrees of freedom become important on a longer time scale. In principle, the TDLDA strength function is infinitely sharp below the ionization threshold, although that is not apparent in the finite-time Fourier transform.

As mentioned earlier, an advantage of the realtime implementation of the TDLDA is that the computing efforts scale with the number of particles *N* and the spatial dimension *D* as $ND \sim N^2$, without requiring any truncation of the space or singling out a particular state. We have examined the scaling of our computation time for the polyenes, which are discussed in detail below. The crosses in Figure 1 show the computation time to set up the ground-state wave function for series ethylene, butadiene, ..., $C_{28}H_{30}$, using 1500 iterations of the Kohn–Sham equations. The abscissa



FIGURE 1. Computation times for the TDLDA method. Shown are the times in minutes for computation of polyenes on the NEC sx4 vector process computer, with an effective speed of 0.4 Gflop, as a function of the number of electrons N in the molecule. Crosses show the time to construct the ground state, taking 1500 iteration steps. Open triangles show the duration of the time evolution phase of the calculation, taking 10,000 iteration steps. Aquadratic N dependence is displayed with the lines.

gives the number of valence electrons in the calculation. The dashed line shows the dependence according to $t \sim N^2$ scaling. One sees that the N^2 scaling applies quite nicely to the larger sized molecules.¹ The computation time for solving the time-dependent equation starting from the ground state is shown by the open triangles in Figure 1. Here we used 10,000 time steps of 0.001 \hbar/eV to obtain the real-time response over an interval of 10 \hbar/eV . From the figure, we see that the scaling is even a little weaker than N.² In fact the number of points *D* needed to represent the wave function scales more slowly than $M \sim N$ due to surface effects.

Polyenes

We first consider the polyenes with alternating double and single bonds which have been studied in empirical models [29] and well as with the linear response [4, 5]. Our structures have bond

 2 However, Ref. [4] quotes a double C—C bond length of 1.544 Å.

lengths of 1.34 Å for C—C bonds and 1.45 Å for double C = C bonds, as is commonly assumed.² The C = C - C and C = C - H bond angles are taken to be 124° and 119°, respectively, in the all-trans conformation. We first discuss a typical case, C_8H_{10} . Figure 2 shows on the left the energies of the π orbitals in the LDA calculation of the ground state. On the right-hand side is the spectrum of the Hückel model, which will be discussed below. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are in the π manifolds indicated in the figure; the HOMO-LUMO energy gap is 2.58 eV in the LDA. The HOMO-LUMO transition has an oscillator strength of $n_e = 5.3$ in the LDA. For comparison, the strength would be $n_e = 8$ if that transition absorbed all of the strength of the π manifold, since there are 8 electrons in the occupied π orbitals.

Next we show in Figure 3 the TDLDA response of C_8H_{10} from zero energy to 30 eV excitation. One sees the strong π - π * transition at 3.86 eV, with a strength $n_e = 3.9$. The slight reduction of strength compared to the single-electron picture is due to the screening effect of the σ electrons. In Figure 3 one also sees the σ - σ * transition as the broad distribution with a concentration of strength



FIGURE 2. C_8H_{10} orbitals with π character. The left-hand side shows the results of the static LDA calculation. The spectrum of the Hückel Hamiltonian with matrix elements given by Eq. (10) is shown on the right. The energies of the Hückel spectrum have been shifted to match the position of the HOMO state.

¹ Our algorithm to construct the ground state requires repeated orthogonalization of the single-particle orbitals, an operation that scales as N^3 . Evidently, the prefactor for this operation is not large enough to make it noticeable.



FIGURE 3. Strength function of C_8H_{10} in the energy region of 0–30 eV, calculated in the TDLDA.

between 15 and 20 eV. This will turn out to be a general feature of the response in conjugated carbon compounds. The strength integrated up to 30 eV is $n_e = 30$; integrating up to 100 eV gives a strength of 41, which compares well to the number of valence electron in C₈H₁₀, namely 42.

We next turn to the systematics as a function of the length of the polyene molecule. Figure 4 shows the HOMO–LUMO gap and the excitation energy of the strong π – π * transition as a function of the number of carbon atoms. With equal atom spacing,



FIGURE 4. Results of the present TDLDA calculation for polyenes, $C_n H_{n+2}$. The HOMO–LUMO gap is shown by the triangles, and the fit to the generalized Hückel Hamiltonian with matrix elements Eq. (10) by the dashed line. For comparison, the n^{-1} dependence similar to Eq. (7) is shown by a dot-dashed line. The energies of the strongest transition in TDLDA are shown by crosses. The strong transition in the PPP empirical theory is shown by the dotted line.

the HOMO–LUMO gap would vary as 1/n, but this is clearly not satisfied for the polyenes. The dashed line is a fit to the generalized Hückel model with two hopping parameters β_s and β_d corresponding to the single and double CC bonds, respectively. For the fit, the parameter values are

$$\beta_s = -2.27 \text{ eV}$$
 and $\beta_d = -2.80 \text{ eV}$. (7)

These are somewhat larger than the values assumed in Ref. [31]. The fit for the finite systems is quite good, showing that rather simple consideration are sufficient to describe the Kohn–Sham single-particle energies. Our fit parameters would give a band gap of 0.86 eV in infinitely long polyene molecules.

The collective transition in the TDLDA has more complex behavior as a function of *n*. The systematics of the energy of the strongest states is shown as the crosses in Figure 4. We have not found a theoretically motivated analytic parameterization for the n dependence of these transitions. The Pariser-Parr-Pople (PPP) empirical Hamiltonian [29], when fitted to the smaller polyenes, gives too high an energy for the largest ones, as is shown by the dotted line in Figure 4. The analytic formula [28] motivated by the plasmon dispersion in one dimension also does not fit well, although it does describe the collective π - π * mode in carbon chains [8]. Possibly the poor analytic fit is due to fragmentation of the collective transition, which occurs in the larger polyenes. This is shown in Figure 5, showing the low-energy TDLDA strength function for N = 8, 18, and 28.

In Figure 6 we show the comparison with experiment and with the RPA calculations of Refs. [4, 5]. The two calculations agree well with each other for the lighter systems, but they diverge for the heavier molecules. Also, the n dependence of the TDLDA results is smoother. In principle, the small-amplitude TDLDA and the RPA are just different mathematical formulations of the same theory, and they should give the same results for the same energy functional. The differences between the LDA functional and the self-consistent (SCF) functional used in the cited references are rather small, and it would be surprising if the effect on the response was the cause of the differing frequencies. The experimental data for polyenes in solution is shown by the crosses and squares. There is also gas-phase data quoted in Ref. [5] which gives 10% higher energies. From Figure 6 one sees good agreement with the lighter polyenes,



FIGURE 5. TDLDA strength function for low-energy transitions in the polyenes with n = 8, 18, and 28.

but the data falls between the two theoretical calculations for the heavier ones. We recently learned of another study of polyenes using TDLDA that obtained a similar finding, that the lowest transition energy is underpredicted [40].

The predicted transition strengths for the two calculations are also significantly different. Figure 7 shows the oscillator strengths in our calculation, compared to the nominal strength in the π manifold. The HOMO–LUMO transition, shown by the triangles, has roughly half the nominal strength. This is further decreased in the TDLDA by two effects. One is the screening by the σ electrons, and the other is the loss of strength in the heavier polyenes to other states. In contrast, the calculation of [5] gave a collective transition with about 75% of the nominal strength for the heavier polyenes. The stronger collectivity then gives a larger upward shift in the energy from the HOMO–LUMO gap position.

As a final example closely related to the polyenes, we examine retinal, the molecule of biological prominence as a retinal chromophore. Retinal is more complicated than a polyene, having an aromatic termination on one end and an carboxyl group on the other, but these play a minor role in the collective longitudinal excitation. We consider the all-*trans* form, which is the final state of the chromophore having absorbed a photon. The ex-



FIGURE 6. Energy of the collective $\pi - \pi^*$ transition in polyenes, comparing theory with experiment. Present TDLDA theory: solid lines; RPA from Ref. [5]; dashes lines. RPA with various energy functionals [13]: filled square. Experimental solution data: crosses [31] and open squares [30]; gas data quoted in Ref. [5]: triangles.



FIGURE 7. Strengths of the collective π - π * transitions in polyenes: single-electron HOMO-LUMO transition, triangles; collective TDLDA transition, crosses. The total strength associated with the π manifold is shown by the dashed line.

perimental data [32] all-trans-retinal shows broad, asymmetric peak with a maximum at 3.2 eV and a full width at half maximum of about 0.6 eV. There is a previous ab initio study using the complete active space SCF (CASSCF) method [33] which we can also compare to. In our calculation, the HOMO-LUMO gap is 2.0 eV, and this state is very strong in the single-electron approximation. The electron-electron interaction in the TDLDA shifts the center of gravity of the strength up to 3.3 eV, close to the experimentally observed position. In contrast, the calculation of Ref. [33] obtained the strong transition at much higher energy. However, as may be seen from Figure 8, the TDLDA strength is fragmented into three states. The LDA predicts the existence of a number of particle-hole states in the 3-eV energy region, and the residual electron interaction is strong enough to mix them. The lowest predicted strong state, at 2.5 eV, is in a spectral region where the empirical absorption strength is small. This is similar to the problem we had with the large polyenes. In the retinal case, however, the situation is complicated by the presence of an oxygen atom on the molecule. As discussed in Ref. [33], the lowest excitation in the molecule has a predominant component with a hole at the oxygen. The transition strength associated with the three strong transition is f = 1.7 in the TDLDA, which is close to the prediction of Ref. [33], but twice our extracted experimental value. That was obtained using the extinction coefficient data of Ref. [32], correcting the solution data by the Debye factor [34].



FIGURE 8. Strength function for retinal; TDLDA, solid; experiment [34], dashed.

Simple Aromatic Molecules

We discuss here the optical absorption spectra of benzene and C_{60} .

BENZENE

Benzene provides our best example of the TDLDA comparisons to experiment. For this calculation, we take the empirical geometry of benzene, D_{h6} symmetry with CC bond length of 1.396 Å and CH bond length of 1.083 Å. The static LDA calculation gives an energy spectrum shown in Figure 9 with a gap Δe of 5.04 eV between the HOMO and LUMO orbitals. The gap may be compared with the empirical energy of the ${}^{1}B_{2u}$ excitation, which is a π - π * particle-hole state having a small residual interaction. That energy is 4.9 eV [35], close to the LDA prediction. Other recent calculations of



FIGURE 9. Benzene orbital energies int eh static LDA. On the far right are the π energies in the Hückel model, with $\beta = 2.52$ eV, shifted to match the HOMO energy.

benzene excitations have been made using the CASSFC method and also with a multireference Møller-Plesset (MRMP) basis [36]. These authors find that the ${}^{1}B_{2u}$ is also well reproduced by the CASFC but not so well by the MRMP.

Turning to the dynamic response, the TDLDA transition strength is shown in Figure 10. One sees the collective $\pi - \pi^*$ state as a narrow peak at 6.9 eV. Thus the residual interaction pushes the π - π * strength up 1.9 eV from its original position at Δe . Above 9 eV there is a broad feature peaking around 18 eV. This is associated with the σ - σ^* transitions; the width is due to the high-level density of particle-hole state in the region of the resonance, and the fact that they are unbound. However, our implementation of TDLDA uses a finite-sized box, which does not give a satisfactory treatment of continuum effects. This spectrum was calculated putting an absorptive boundary condition on the wave function at the edge of the box. Instead of the very fine structure predicted with a reflecting boundary condition, the absorptive condition produces (probably spurious) broader structures.

To compare with the empirical strength function, we consider data reported in two experiments. In Ref. [35], the absolute strength was mea-



FIGURE 10. Optical absorption of the benzene molecule (in units of eV^{-1} : (a) experimental, from Ref. [37]; (b) TDLDA. An absorptive potential has been put at the boundaries of the grid to mimic the continuum. The grid has the shape of a sphere of radius 7 Å with $\Delta s = 0.3$ Å and $\Delta t = 0.001 \hbar / eV$. The number of spatial mesh points is about 50,000. The figure shows the Fourier transform of real-time response over a time $T = 30 \hbar eV$.

sured for excitation energies up to about 10 eV. There is a quite sharp state at 6.9 eV in very good agreement with our predicted π - π * transition. Comparing with the other theoretical methods, the energy is well reproduced by the MRMP but not the CASSCF [36]. The empirical strength of the integrated peak from 6.5 eV up to the minimum at 8.3 eV is f = 0.9 eV. This agrees well with our theoretical strength for the collective transition, f = 1.1. There both the CASSCF and MRMP give even better agreement with experiment. We mentioned that none of the theory describes the finer details of the absorption spectrum in the 7-eV excitation region. Besides the rather sharp state there is a broader plateau that may be associated with the forbidden ${}^{1}B_{1u}$ electronic excitation coupled to an e_{2g} C–C stretch vibration. The experimental strength function also shows very fine peaks in the neighborhood of the ionization energy. These are Rydberg states which are beyond the reach of simple energy densities functions, which lack the Coulomb tail in the mean field. Another experiment [37] reported the absorption strength going up to much higher energies, but without an absolute normalization. In Figure 10 we show this data normalized to our calculation. We see that broad σ - σ^* feature is reproduced in position and width very well. However, there is no hint of the finer structure found in the TDLDA strength function.

C₆₀

Our last example is the molecule C_{60} . This molecule has been well studied in the LDA; the predicted HOMO-LUMO gap is 1.65 eV, compared with the measured gap of ~ 1.6 eV. The strength function computed with the TDLDA is shown in Figure 11. We see a set of strong transitions in the region of 4-7 eV excitation, and a much larger and broad set in the region of 15-30 eV. The lower transitions have a π - π * character. Experimentally, the absorption strength below 6 eV has been measured in absolute terms and the data is reviewed in Ref. [38]. Comparison of theory and experiment is made in Table I. There is a good correspondence between the TDLDA transition at 3.4 eV and the observed state at 3.8 eV. For the higher transitions, theory predicts more strong states than the number of peaks observed, so there is no one-to-one correspondence. However, the overall strength distribution comes out fairly well. This may be seen in Figure 12 comparing the



FIGURE 11. Strength for C₆₀ calculated in the TDLDA.

TDLDA E(eV)	TDLDA f	Experiment E(eV)	Experiment f
3.4	0.3	3.8	0.5
4.3	0.9		
5.3	2.5	4.8	2.1-2.5
6.0	2.5	5.8	5-6
6.6	1.1		



FIGURE 12. Integrated strength below 6.2 eV in C₆₀. TDLDA, dashed line; RPA from Ref. [41], dotted line; experiment from Ref. [38], solid line.

integrated strength distribution up to 6.2 eV. Of course the TDLDA strength is sharply peaked without the line-broadening processes that would be computable in a more complete theory. The total strength in the region comes out about right in TDLDA, but shifts of the order of 0.5 eV would be required to fit the data.

The higher spectral region again shows a broad peak from the σ - σ * transitions, here centered in the 20–25 eV range. The only data in this region is the photoelectron cross sections [39]. It shows a peak at 20 eV having a full width at half maximum of about 10 eV, consistent with the TDLDA results. It would be interesting to know whether the additional predicted structure at 10–13 eV is present physically as well.

Conclusion

The TDLDA is an attractive theory for collective excitations in large molecules because of its conceptual simplicity, automatic compliance with sum rules, and favorable scaling behavior for large molecules. We have found it competitive with other methods as far as the maximum size one calculates, and it produces the entire spectrum at once. We have found it to be rather good for conjugated carbon molecules, giving a reasonable account of the strong transitions in both the π - π * and σ - σ * manifolds of states.

Much effort has been devoted recently to the construction of improved energy functionals. References [11] and [13] in particular have examined the differences in the results with so-called generalized gradient approximations. The effects appear to be small on the scale of the intrinsic validity of the TDLDA. On the other hand it appears to be very important to include an unrestricted space of wave function that is guaranteed to satisfy the oscillator strength sum rule in order to produce converged excitation energies for the strong collective modes.

Of course, the numerical effort is still large in these calculations, and it is useful to extract information about the validity of simpler theories. In the π - π * manifold, the energetics of the underlying single-particle states are fairly well described by the Hückel Hamiltonian. The results are summarized in Figure 13, showing the deduced hopping matrix elements as a function of the CC bond length. Fitting the conjugated molecules to a power



FIGURE 13. Effective Hückel matrix elements in the molecules studied. They are, in ordering of increasing bond length: polyene single bond, benzene, and polyene double bond.

law dependence on bond length, the extracted matrix elements vary as $t \sim r^{-2.7}$. This is a stronger dependence than the commonly assumed form, $t \sim r^{-2}$. The matrix element for the carbon chain molecules is quite different, perhaps because of the absence of hydrogen atoms. As is well known, the electron-electron interaction strongly perturbs the absorption strength function. In the region of the π - π^* transitions, the strength is shifted upward by an amount of the order of 1–2 eV for the systems studied. In the case of carbon chains, the transition energy can be described fairly well analytically. The energies agree well with the empirical values for the smaller molecules, but the larger ones are predicted to have more fragmentation of strength in the TDLDA than is observed. The amount of strength in the π - π * transition in principle depends on the coupling to the other electrons. In small or extended molecules the coupling is weak; the resulting screening is no more than a factor of 2. On the other hand, in C_{60} the π - π * transition strength is more strongly screened. The absorption spectra typically have a gap above the strong π - π^* transition, follows by a dense spectrum of σ - σ * transitions above 10 eV. This spectrum peaks in the range of 15-20 eV and is quite broad. This feature is present in the empirical absorption, but quantitative experimental data is only available for one case, benzene. There we found good agreement on the overall shape and size of the σ - σ^* absorption peak. In view of the

evident success of the TDLDA theory, it would be interesting to consider more ambitious applications. One direction is to try other, more difficult, elements. In particular, it may be possible to treat *d*-shell elements with mesh sizes of the order of $\Delta x \approx 0.2$ Å, which would allow small molecules and clusters to be calculated. Another direction would be to study the effect of perturbations on the spectra. Possible perturbations include nearby charges or nearby molecules, thermal distributions of ionic geometries, and electron vibration coupling.

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