

Jacob's ladder for time-dependent density-functional theory: Some rungs on the way to photochemical heaven

Mark E. Casida[†]

*Laboratoire d'Etudes Dynamiques et Structurales de la
Sélectivité (LEDSS), Laboratoire UJF-CNRS (UMR 5616),
Université Joseph Fourier (Grenoble I), 38041 Grenoble, FRANCE*

The time-dependent extension of density-functional theory (TDDFT) provides a rigorous formalism allowing the treatment of electronic excitations and excited states. However, just as in traditional (ground-state) density-functional theory (DFT), the quality of the results depends upon the approximation used for the unknown exchange-correlation (xc) functional. Perdew and Schmidt have described the various functionals developed for ground state DFT in terms of a Jacob's ladder, where the rungs correspond to successive levels of approximation of the xc-functional[1]. Within the adiabatic approximation, these functionals can also be used in TDDFT. However, TDDFT places additional demands on the functional that are not typically satisfied by approximations developed for the ground-state. The simple time-dependent local approximation already gives remarkably good results for many excited states. However other excitations require more accurate treatment of the xc potential. Our work on this problem will be summarized in terms of a “Jacob's ladder” adopted to the special needs of applied TDDFT.

Long accepted as an important fundamental theoretical tool in solid state physics, density-functional theory (DFT) has now also come to be accepted as an important fundamental tool

[†]Electronic address: `Mark.Casida@ujf-grenoble.fr`

in the quantum chemistry community. The 1998 Nobel Prize in Chemistry awarded “to Walter Kohn for his development of the density-functional theory and to John Pople for his development of computational methods in quantum chemistry” certainly emphasized this acceptance [2]. In comparison with *ab initio* methods, DFT has the important advantage that it includes electron-correlation effects in a simple Hartree-Fock (or Hartree-like) manner. When suitably programmed, this allows DFT to be applied to larger molecules, and hence to more molecules of practical importance, than is the case with traditional *ab initio* methods. It is also simple enough for on-the-fly calculation of forces needed in so-called *ab initio* molecular dynamics methods (most of which are based on DFT), such as that of Car and Parrinello [3]. Nevertheless, with all its advantages, traditional Hohenberg-Kohn-Sham DFT [4, 5] was born an incomplete theory, limited to calculating the energy and charge density for the static ground electronic stationary state. Here I review the time-dependent generalization of DFT, and particularly how different levels of sophistication of functionals can be important for time-dependent DFT (TDDFT) calculations of electronic excited state potential energy surfaces.

To the extent that we can solve the “problem of the unknown functional” in TDDFT, we can look forward to an ever widening list of applications. Since our formulation [6] and implementation [7] of TDDFT in a manner suitable for molecular applications, some form of TDDFT has been implemented in nearly every major quantum chemistry program. Most applications have been to the calculation of electronic excitation energies and spectra, including for chlorophyll a [8], fullerenes [9], polyacetylenes [10–13], transition metal coordination compounds [14–16], and phototoxic drugs [17]. Nevertheless there have now been several calculations of potential energy surfaces [18–23] and the implementation of analytic derivatives for TDDFT [24, 25] has allowed automatic geometry optimizations to be carried out for excited states. These developments make me optimistic that we will soon see some type of Car-Parrinello treatment of a photodynamics problem. Certainly first attempts are already being made in this direction. These include Car-Parrinello for a single excited state using the multiplet sum formalism [26] and implementation of TDDFT to take into account finite temperature vibrational structure for excitation spectra in Car-Parrinello codes [27]. Very recent work of relevance to this problem is also being carried out in the R  thlisberger group [28].

In the remainder of this chapter, I first review the status of the treatment of excited states in DFT and then go into a detailed analysis of where and how functionals can be improved.

I. EXCITED STATES IN DFT

Traditional DFT is based upon two theorems due to Hohenberg and Kohn [4]: (1) For a nondegenerate system of electrons in its *ground stationary state* the charge density determines the external potential up to an arbitrary additive constant. (2) In principle, the *ground state* energy and charge density may be obtained by minimizing a certain functional $E[\rho]$ (for which a practical exact form is unfortunately not known.) I have deliberately emphasized the references to “ground” and “stationary state.” Before seeing how we can generalize the traditional theory to get around these limitations, it is useful to review the status of “ordinary” DFT.

In practice, the Kohn-Sham formulation [5] of DFT is almost always used. This overcomes the major difficulty with finding a density-functional for the kinetic energy by introducing a set of orthonormal auxiliary functions (i.e. the Kohn-Sham orbitals), ψ_i with occupation numbers f_i , which sum to the ground state density,

$$\rho(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2, \quad (\text{I.1})$$

and allow us to express the ground state energy as

$$E = \sum_i f_i \langle \psi_i | \hat{h}_{core} | \psi_i \rangle + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho]. \quad (\text{I.2})$$

These orbitals are to be found by minimizing the energy subject to the orthonormality constraint.

The result is the Kohn-Sham equation,

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (\text{I.3})$$

Since no practical exact form of the exchange-correlation functional

$$E_{xc}[\rho] = \int \epsilon_{xc}[\rho](\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \quad (\text{I.4})$$

is known, it is approximated in practice. There are several levels of sophistication that can be used for constructing approximate functionals. Recently, Perdew and Schmidt[1] have organized the different families of density functionals into a “Jacob’s ladder of density functional

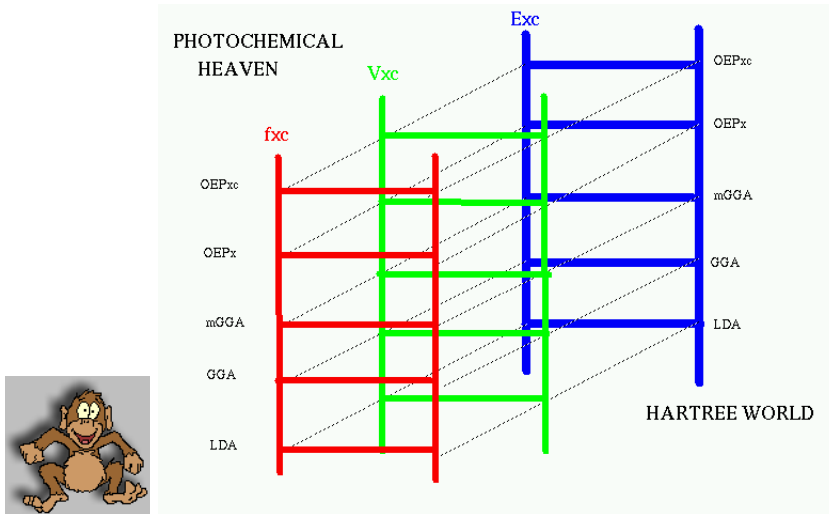


FIG. 1: Jacob’s jungle gym for TDDFT.

approximations.” A generalization of this ladder is given in Fig. 1. The lowest level represents the simplest approximation which is the local density approximation (LDA) in which the exchange-correlation energy density is approximated by that of the homogeneous electron gas (HEG),

$$\epsilon_{xc}[\rho](\mathbf{r}) = \epsilon_{xc}^{HEG}(\rho(\mathbf{r})). \quad (\text{I.5})$$

This works remarkably well, especially for properties such as ionization potentials and molecular geometries of “ordinary” molecules. It is normally used in its spin-dependent form (the local spin density approximation), but for simplicity I will neglect spin except where it is explicitly necessary to include it. Unfortunately the LDA tends to overbind. The next level of approximation are the generalized gradient approximations (GGAs) which include an explicit dependence on the reduced gradient of the charge density, $x(\mathbf{r}) = |\vec{\nabla}\rho(\mathbf{r})|/\rho^{4/3}(\mathbf{r})$. Well-constructed GGAs are able to give significantly better chemical binding energies. The third level of approximation is the meta-GGAs which include a dependence on the kinetic energy density, $\tau(\mathbf{r}) = \sum_i f_i |\vec{\nabla}\psi_i(\mathbf{r})|^2$. Older and more explored is the fourth level of the ladder (labelled OEPx here) in which some explicit dependence on occupied orbitals is included, typically through some portion of Hartree-Fock exchange. This inclusion of an orbital dependence in the density-functional may seem a little strange, until it is recalled that the orbitals themselves are implicit functionals of the charge density. These hybrid functionals were introduced because they are able to give near chemical

accuracy for thermochemistry — something which GGAs alone were unable to do. The highest level of the ladder (OEPxc) includes also a dependence on the unoccupied orbitals. At this level, we have enough degrees of freedom to construct “exact” exchange-correlation potentials from *ab initio* theory, giving rise to the term “*ab initio* density-functional theory” [29]. Work at this level is only just beginning. The reader is referred to the book by Koch and Holthausen for a property-by-property assessment of the accuracy of many popular functionals [30].

In thinking about the impact of a particular choice of functional on any given property, it is important to realize that the historical emphasis in creating approximate density-functionals has been to obtain accurate total energies. Hence most work has concentrated on understanding and approximating the exchange-correlation *energy*, $E_{xc}[\rho]$. As we go to higher and higher functional derivatives of the exchange-correlation energy, less and less is known about their exact properties and how to approximate them. Since the exchange-correlation *potential*, $v_{xc}[\rho](\mathbf{r}) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$, enters into the orbital equation, it has a direct effect on the charge density. It also enters into the calculation of analytic first-derivatives used in automatic geometry optimizations. These are important properties and more and more effort is being made to find better approximations for the exchange-correlation potential [18, 31–33, 33–37]. The second derivative is the exchange-correlation *kernel*, $f_{xc}[\rho](\mathbf{r}, \mathbf{r}') = \delta^2 E_{xc}[\rho]/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')$. It is needed for the calculation of static response properties such as electronic dipole polarizabilities and for the calculation of analytic second-derivatives. We can, of course, go on taking derivatives, but this is high enough for present purposes.

Excited States. It is interesting to note that the first Hohenberg-Kohn theorem implies that the ground state charge density, by determining the external potential up to an additive constant, also implicitly determines the entire manifold of electronic ground and excited states up to an arbitrary energy zero. The problem has been how to find a practical approximate scheme for treating excited states based on either (or both) the ground and excited state charge densities. Several methods have been proposed for doing this (see Ref. [21] for a recent review.) Practical calculations typically use one of two approaches: either (i) the DFT Δ SCF approach or (ii) TDDFT. Both approaches have advantages and disadvantages and until the two are united into a single formalism, we must learn to pick and choose depending upon our application.

The Δ SCF approach is historically the older of the two approaches. It is based on the idea that DFT should be valid for the lowest state of each symmetry (especially if the state is well described by a single-determinantal wave function!) If this is true, it suffices to take the energy difference of two SCF calculations with different orbital occupancies. This approach is formally exact for the first ionization potential of a molecule (but is often also useful for other ionization potentials). It is also exact for the lowest excited state of a given symmetry (and it is very commonly applied in this form to calculate the lowest triplet state of a closed-shell molecule). In more complicated situations, *afficionados* of the Δ SCF approach use the Ziegler-Rauk-Baerends multiplet sum method[38, 39] to *estimate* energies for excited states. In this variation on the Δ SCF method, first-order energies of multi-determinantal states are estimated by a weighted sum of the energies of single-determinantal states based upon a group theoretical guess of the form of the multi-determinantal wave function. In the case of a singlet one-electron excited state of a closed-shell molecule,

$$E_{i \rightarrow a}^{singlet} \cong 2E_{i\downarrow \rightarrow a\downarrow} - E_{i\downarrow \rightarrow a\uparrow} . \quad (\text{I.6})$$

The *strength* of the Δ SCF approach is that it can handle two-electron and higher-electron excited states easily. The *weakness* of Δ SCF lies in its lack of formal justification (except for particular special situations, such as the first ionization potential), and in its inability to handle nontrivial configuration mixing, such as would be encountered, say, near avoided crossings of two excited states.

Time-dependent density-functional theory operates very differently. Although TDDFT was initially viewed as an *ad hoc* method, a substantial body of work has now given it a rigorous formal footing [40–48] (see especially reviews by Gross and co-workers [49–51].) In analogy with experiment, TDDFT excitation energies are determined by finding the resonant frequencies for the response of the charge density to a time-dependent electric field (*think photon!*). The *strength* of TDDFT is that it is formally well-founded (though there is an unknown functional) and configuration mixing in excited states emerges as a natural consequence of the formalism. The *weakness* of TDDFT in practice is in the functionals and in the adiabatic approximation

which restricts it to one-electron excitations. Practical calculations solve the equation,

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} = \omega_I \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix}, \quad (\text{I.7})$$

where

$$A_{ia\sigma,jb\tau} = \delta_{i,j}\delta_{a,b}\delta_{\sigma,\tau}(\epsilon_{a\sigma} - \epsilon_{i\sigma}) + K_{ia\sigma,jb\tau} \quad (\text{I.8})$$

$$B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}, \quad (\text{I.9})$$

and the “coupling matrix,”

$$K_{ia\sigma,jb\tau} = \int \int \psi_{i\sigma}(\mathbf{r})\psi_{a\sigma}(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}^{\sigma,\tau}(\mathbf{r}, \mathbf{r}') \right) \psi_{j\tau}(\mathbf{r}')\psi_{b\tau}(\mathbf{r}') d\mathbf{r}d\mathbf{r}'. \quad (\text{I.10})$$

Thus the excitation energy, ω_I , depends upon both the exchange-correlation potential through the orbitals, $\psi_{i\sigma}$, and orbital energies, $\epsilon_{i\sigma}$, and on the exchange-correlation kernel, $f_{xc}^{\sigma,\tau}(\mathbf{r}, \mathbf{r}')$.

Had the adiabatic approximation *not* been made, then the exchange-correlation kernel would also have a frequency dependence, $f_{xc}^{\sigma,\tau}(\mathbf{r}, \mathbf{r}'; \omega)$. The adiabatic approximation assumes that the exchange-correlation potential, $v_{xc}^\sigma(\mathbf{r}, t)$, reacts instantly to any temporal change in the charge density. The exact theory includes “memory effects” whereby the response of the potential at time t depends not only on the charge density at time t but also on the charge density at previous times. In principle the adiabatic approximation is valid only in the low frequency (i.e. low energy = $\hbar\omega$) limit. In practice, the limit of validity of the adiabatic approximation can only be determined through explicit calculation and comparison with reliable experimental and theoretical results.

Jacob’s Jungle Gym. Potential energy surfaces can be calculated by adding the excitation energies from TDDFT directly to the total ground state energy obtained from traditional DFT. This transforms the problem of Jacob’s ladder into that of Jacob’s jungle gym (Fig. 1) because we can expect to need reasonably high-quality approximations for both the exchange-correlation energy and for its functional derivatives. In particular, the ground state energy depends heavily on the approximation for E_{xc} and also to some extent on the quality of the first functional derivative, v_{xc} . The excitation energy, ω_I depends on v_{xc} and also on f_{xc} .

Nevertheless, we can do surprisingly well on the lowest level of the jungle gym, which is known as either the time-dependent local density approximation (TDLDA) or as the adiabatic local

TABLE I: Adapted from Ref. [7].

N ₂ Vertical Excitation Energies (eV)				
State	TDLDA	Expt	TDHF	CIS
Singlet \rightarrow Singlet Transitions				
$w^1\Delta_u$	10.22	10.27	8.75	9.09
$a'^1\Sigma_u^-$	9.66	9.92	7.94	8.51
$a^1\Pi_g$	9.10	9.31	9.76	9.60
Singlet \rightarrow Triplet Transitions				
$C^3\Pi_u$	10.36	11.19	11.26	11.85
$B'^3\Sigma_u^-$	9.66	9.67	7.94	8.51
$W^3\Delta_u$	8.83	8.88	5.80	7.35
$B^3\Pi_g$	7.60	8.04	7.62	7.94
$A^3\Sigma_u^+$	7.88	7.75	3.47	6.25
Average Error for All Eight States				
	0.25		1.69	1.02

density approximation (ALDA). Experience has shown that one should expect excitation energies which are better than those given by the time-dependent Hartree-Fock (TDHF) approximation or by configuration interaction singles (CIS) for comparable or less effort *provided*, (i) excitations are vertical and at the ground state equilibrium geometry, (ii) only excitation energies are considered which are below the TDDFT ionization threshold at minus the HOMO orbital energy, and (iii) there is not too much change in the charge densities before and after the excitation process. TDLDA results for N₂ are given in Table I.

II. LADDER-BY-LADDER ANALYSIS

In this section I will show several instances where it is necessary to mount the various ladders in Jacob's jungle gym, beginning with the E_{xc} ladder and continuing on to the f_{xc} ladder.

Problems with E_{xc} . Since TDDFT is based on the response of the ground state, it fails when the description of the ground state fails. A classic example of such a failure is the DFT

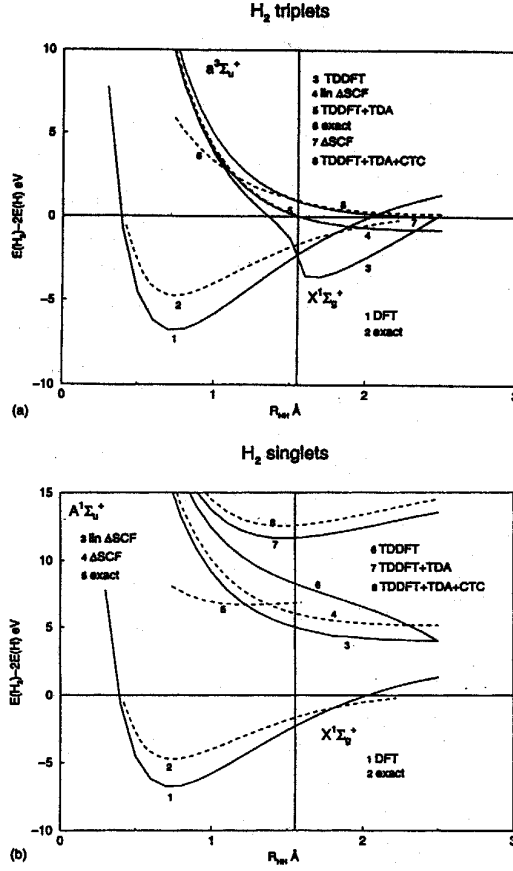


FIG. 2: H₂ (a) ground and triplet excited state surfaces. (b) ground and singlet excited state surfaces. Adapted from Ref. [22].

description of the ground states of biradicals. This problem is illustrated for the simple hydrogen molecule in Fig. 2. A similar problem is encountered for rotating around a double bond.

Figure 2 can be understood beginning from an analysis of symmetry breaking in the ground-state [52]. The stability of the Kohn-Sham wave function with respect to symmetry-breaking can be tested by considering an arbitrary unitary transformation of the orbitals,

$$\psi_r^\lambda(\mathbf{r}) = e^{i\lambda(\hat{R}+i\hat{I})}\psi_r(\mathbf{r}), \quad (\text{II.1})$$

where \hat{R} and \hat{I} are real operators. After a fair amount of algebra, one arrives at the energy

expression,

$$E_\lambda = E_0 + \lambda^2 \left[\vec{R}^\dagger (\mathbf{A} - \mathbf{B}) \vec{R} + \vec{I}^\dagger (\mathbf{A} + \mathbf{B}) \vec{I} \right] + \mathcal{O}(\lambda^3), \quad (\text{II.2})$$

where matrix elements of the \hat{R} and \hat{I} operators have been arranged in column vectors and the $\mathcal{O}(\lambda)$ term disappears because the energy has already been minimized before considering symmetry-breaking. The presence of the terms $(\mathbf{A} \pm \mathbf{B})$ shows the connection with the pseudo-eigenvalue problem (I.7). In fact, Eq. (I.7) can be rewritten as the eigenvalue equation

$$(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})\vec{Z}_I = \omega_I^2 \vec{Z}_I. \quad (\text{II.3})$$

Assuming that the *aufbau* principle is obeyed, the matrix $(\mathbf{A} - \mathbf{B})$ is always positive definite. However $(\mathbf{A} + \mathbf{B})$ may have negative eigenvalues. In that case, the energy E_λ will fall below E_0 for some value of \vec{I} . At the same time, this will correspond to a negative value of ω_I^2 (i.e. an imaginary value of ω_I .) This is exactly what happens in Fig. 2. At the bond distance given by the vertical line, the Kohn-Sham energy can be further lowered by allowing for different orbitals with different spin, though these orbitals no longer belong to proper representations of the molecular symmetry group. This is a disaster for calculating excited state surfaces because the triplet excitation energy falls to zero and then becomes imaginary. We might have hoped that the excitation energy would remain reasonable until fairly close to the symmetry breaking point, however Fig. 2 shows that we actually have a problem significantly before symmetry breaking occurs. (A stability analysis for the Kohn-Sham equation was also carried out by Bauernschmitt and Ahlrichs [53], but no connection was made with TDDFT excitation energies.)

In the absence of the exact exchange-correlation functional, the ultimate solution to the symmetry-breaking problem is probably some sort of multi-determinantal generalization of DFT for the groundstate. However it is interesting to note that the Δ SCF approach is in principle valid for the lowest triplet state of H_2 and the excitation energy curve is in fact quite reasonable. So one way to try to improve the TDDFT excitation energy curves is to try to incorporate some features of the Δ SCF approach. We have done this in Ref. [22]. We find that, loosely speaking, 90% of the solution to this problem comes from using the Tamm-Dancoff approximation (TDA) which consists of setting $\mathbf{B} = \mathbf{0}$. The resultant equation for excitation energies,

$$\mathbf{A}\vec{X}_I = \omega_I \vec{X}_I, \quad (\text{II.4})$$

TABLE II: Adapted from Refs. [54] and [36].

Molecule	Ionization Potential (eV)			
	$-\epsilon_{HOMO}^{LDA}$	$-\epsilon_{HOMO}^{AC-LDA}$	ΔSCF	Expt
N ₂	10.36	15.36	15.62	15.60
CO	9.10	13.78	14.10	14.01
CH ₂ O	6.32	10.85	10.92	10.88
C ₂ H ₄	6.91	11.01	10.94	10.68

decouples the excitation energy problem from the problem of the stability of the ground state wave function. Results for H₂ are shown in Fig. 2. A second part of the solution is a *charge transfer correction* (CTC) [22],

$$A_{ia\sigma,ia\sigma} \leftarrow A_{ia\sigma,ia\sigma} + \omega_{i\sigma \rightarrow a\sigma}^{\Delta SCF} - \Delta \epsilon_{i\sigma \rightarrow a\sigma}. \quad (\text{II.5})$$

As shown in Fig. 2, the TDDFT+TDA+CTC triplet curve is virtually identical to the ΔSCF triplet curve. In the singlet case, the ΔSCF method is hard to justify and indeed the excited singlet curve seems to be dissociating to the wrong limit, while the TDDFT+TDA+CTC singlet curve is at least qualitatively correct.

Problems with v_{xc} . Consider now just vertical excitation energies near the equilibrium ground state geometry. It can be shown that the TDDFT ionization threshold is at $-\epsilon_{HOMO}$ [54]. As illustrated in Table II, this threshold is too low. The reason is known and is because the asymptotic behavior of v_{xc} for nearly all common functionals falls off too quickly, leading to underbinding. Unless this is corrected, TDDFT excitation energies calculated with an extended basis set will show variational collapse. As in Fig. 3, TDLDA excitation energies above $-\epsilon_{HOMO}^{LDA}$ collapse because we are trying to describe with a finite basis set a continuum which has set in too early. A very simple correction of the asymptotic behavior of the potential is,

$$v_{xc}^{AC-LDA}(\mathbf{r}) = v_{xc}^{LDA}(\mathbf{r}) - \min(IP_{\Delta SCF} + \epsilon_{HOMO}, \beta \rho_{\sigma}^{1/3} \frac{x_{\sigma}^2}{1 + 3\beta x_{\sigma} \sinh^{-1} x_{\sigma}}), \quad (\text{II.6})$$

where x_{σ} is the reduced gradient defined earlier. (Since the correction is just a rigid shift of the potential except at large r , the density and total energy remain largely unaffected.) The resultant ionization potentials are shown in Table II. Figure 3 shows that this does indeed fix

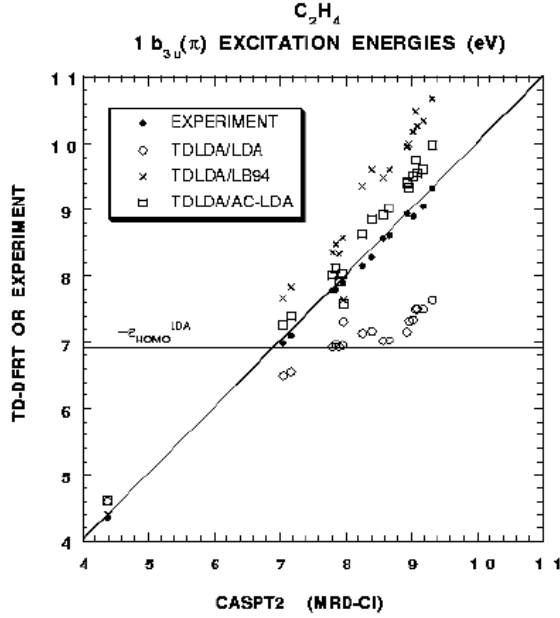


FIG. 3: Variational collapse of ethylene π excitation energies of above the TDLDA ionization threshold at $-\epsilon_{HOMO}^{LDA}$. From Ref. [36].

the problem of variational collapse. Since this allows us to treat higher excited states such as Rydberg states, it also allows us to treat avoided crossings between valence-type and Rydberg-type excitations, such as those in the 1A_1 manifold of CH_2O [18].

Ethylene is an important molecule for photochemistry, so it is important to describe its excited states as well as possible. While correcting the asymptotic behavior of v_{xc} helps immensely in the TDDFT description of higher π excited states, we have noticed that certain excitations out of the σ manifold of orbitals are too low in TDDFT [54]. This is particularly problematic because these σ excitations mix artifactually with the π excitations around 8 eV to give a false

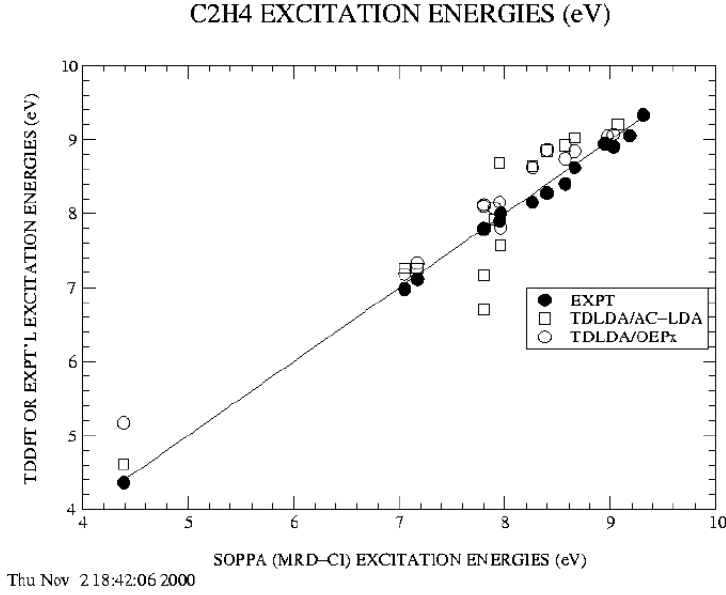


FIG. 4: Comparison of *all* one-electron excitation energies of C_2H_4 with those from good *ab initio* calculations.

picture of the nature of the excited states (Fig. 4). We have traced this back to problems with the relative energies of the occupied σ and π orbitals[36], by using the fact that the TDA is often a good approximation near the ground state equilibrium geometry and that relaxation is often relatively small in DFT. This latter point makes DFT very different than Hartree-Fock. It is well-known that Hartree-Fock orbitals are ill-adapted for describing the excitation process because the unoccupied orbitals see one more electron than do the occupied orbitals. In contrast, DFT orbitals are much better adapted to describing the excitation process because the occupied and unoccupied orbitals see the same potential. Thus, as long as the charge density remains roughly the same for the initial and final states and we are not near an avoided crossing where there are nontrivial configuration mixing effects, the excitation can be described in terms of a simple two-level model (2LM) as a single promotion $\psi_i \rightarrow \psi_a$ plus singlet and triplet spin coupling. Within the 2LM+TDA, it can be shown that,

$$\omega_T \leq \Delta\epsilon \leq \omega_S \quad (\text{II.7})$$

and the singlet-triplet splitting gets smaller as we go to Rydberg states[36]. This and Table III allow us to see that the problem in ethylene with TDDFT excitations out of the σ system

TABLE III: $\text{C}_2\text{H}_4 \ ^{1,3}B_{1g}[1b_{3g}(\pi'_{CH_2}), 1b_{2g}(\pi^*)]$ Excitation Energies (eV). Adapted from Refs. [36] and [55].

Method	ω_T	ω_S	$\Delta\epsilon$
TDLDA/LB94	6.59	7.08	6.83
TDLDA/AC-LDA	6.70	7.16	6.92
TDLDA/LDA	6.93	6.98	7.19
$\Delta\text{SCF/LDA}$	7.13	7.19	7.52
TDLDA/OEPx	8.1	8.46	8.34
Expt		9.2	
TDHF		9.22	
CIS	8.56	9.28	
CIS-MP2	8.96	9.31	

of ethylene lies at the orbital energy level, at least in the case of the $1b_{3g}(\pi'_{CH_2}) \rightarrow 1b_{2g}(\pi^*)$ excitation (the $1b_{3g}(\pi'_{CH_2})$ looks like an in-plane π^* -like arrangement of CH sigma bonds.) In particular, with the LDA, LB94, and AC-LDA functionals, the simple orbital energy difference lies *significantly lower* than the expected triplet excitation energy around 8.5 eV.

This indicates that v_{xc} is not only incorrect in the large r region, but is also subtly incorrect in regions of space important for occupied orbitals. In order to solve this problem, it suffices to calculate a more accurate potential. According to Kohn and Sham[5], the exact exchange-correlation potential is simply that which satisfies the condition that the *difference* of the charge densities is zero:

$$0 = \Delta\rho_\sigma(\mathbf{r}) = \rho_\sigma^{\text{exact}}(\mathbf{r}) - \rho_\sigma^{\text{DFT}}(\mathbf{r}). \quad (\text{II.8})$$

This is almost the same in the exchange-only case as the optimized effective potential which is defined by requiring that the *linear response* of the charge density is zero,

$$0 = \delta\rho_\sigma(\mathbf{r}) = \int \int (\Sigma_x^\sigma[\gamma_{\text{DFT}}](\mathbf{r}; \mathbf{r}') - v_x^\sigma(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')) \gamma_{\text{DFT}}^\sigma(\mathbf{r}'; \mathbf{r}) d\mathbf{r} d\mathbf{r}', \quad (\text{II.9})$$

where $\hat{\Sigma}_x^\sigma$ is the HF exchange potential. Equivalently v_x^σ is the multiplicative potential whose orbitals minimize the HF energy expression [56, 57]. We have programmed and carried out

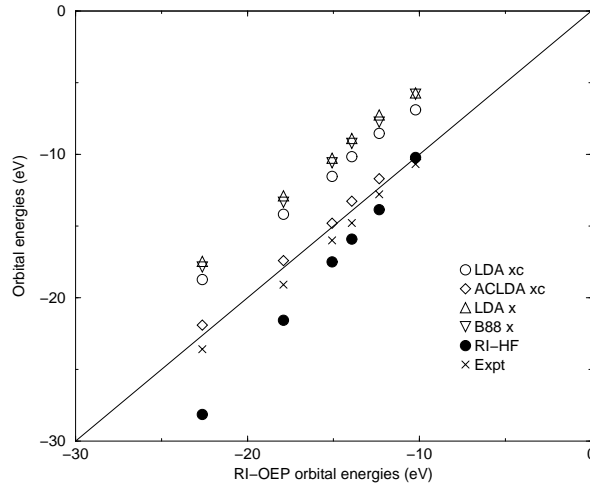


FIG. 5: Correlation graph between various exchange, exchange-correlation methods, and OEP for C_2H_4 : all 6 occupied valence orbitals. From Ref. [55].

exchange-only OEP calculations for molecules within a resolution-of-the-identity methodology, without use of 4-center integrals [55]. To be fair, these calculations entail numerous subtle numerical difficulties [55, 58], but we are reasonably confident about the quality of the results presented here. Figures 5 and 6 show what happens to the orbital energies in C_2H_4 . In both cases, the simple AC-LDA gives orbital energies in reasonably good agreement with our OEP calculations. However the small relative differences for the σ and π orbitals are important, bringing the OEP orbital energy difference in Table III much more in-line with the expected value. Figure 4 shows that although our TDLDA/OEPx calculations have neglected correlation in v_{xc} (though not in f_{xc}) we are, as hoped, able to clean up the structure of the excited states around 8 eV.

Problems with f_{xc} . As mentioned earlier, the adiabatic approximation is a low frequency (low energy) approximation. It is thus natural to ask how and where the frequency dependence of f_{xc} should become important. Two rather different types of frequency dependence are important in this context [59]. The first type (dispersion) consists of a continuous variation of $f_{xc}(\omega)$ as a function of ω , and will result in shifted excitation energies. The second type (pole structure) consists of the probable presence of singularities in $f_{xc}(\omega)$ at particular values of ω . This pole structure is associated with the appearance of additional satellite peaks in the electronic absorption spectra, due to mixing of many-electron with one-electron excitations.

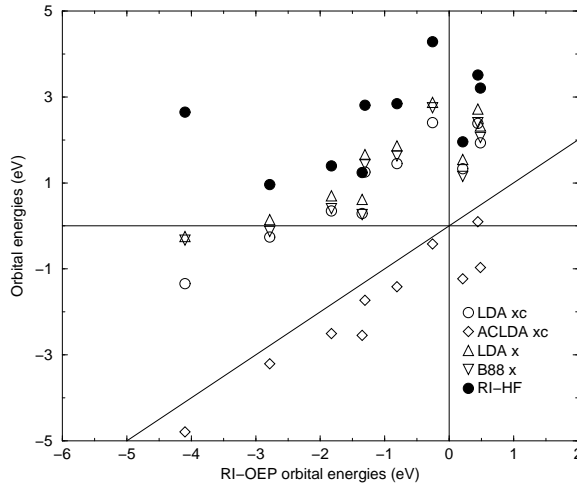


FIG. 6: Correlation graph between various x-only method and OEP for C_2H_4 : 10 unoccupied orbitals. From Ref. [55]

The development of useful exchange-correlation kernels which go beyond the adiabatic approximation has been a slow process, but a recent application of one such kernel to semiconductors is encouraging [60]. I will give a brief overview of some of the principal work leading up to this recent application. The first attempt at a frequency-dependent exchange-correlation kernel was given by Gross and Kohn [61]. Almost a decade later, Dobson proved the harmonic potential theorem (HPT) which must be obeyed by any admissible $f_{xc}(\omega)$ [62]. He showed that the adiabatic approximation satisfies the HPT but that the suggestion of Gross and Kohn does not. Vignale gave a general condition guaranteeing that exchange-correlation functionals obey the HPT [63]. Vignale and Kohn [64] showed that the exchange-correlation potential in TDDFT is an intrinsically nonlocal functional of the charge density which does not admit a gradient expansion, unless the theory is reformulated to also include a dependence on the current density, $\vec{j} = (1/2i) \sum_i f_i (\psi_i^* \vec{\nabla} \psi_i + \psi_i \vec{\nabla} \psi_i^*)$. They gave an explicit form for the exchange-correlation functional in the case of a perturbation of the homogeneous electron gas which is slowly varying on the scales of k_F^{-1} (\sim interelectron distance) and v_F/ω (\sim distance traveled by an electron during a period of the perturbing field.) Vignale, Ullrich, and Conti reformulated the Vignale-Kohn theory in terms of the exchange-correlation viscoelastic stress tensor [65]. Dobson, Büchner, and Gross have presented a generalization of the Vignale-Kohn theory [66]. In order to apply these theories, one must also know the frequency dependence of $f_{xc}(\omega)$ for the homogeneous electron

gas. This has been studied by Nifosì, Conti, and Tosi [67]. The exchange-correlation kernel for the homogeneous electron gas is a relatively flat function of frequency at low frequency, varies more rapidly as the plasmon frequency is approached, and has a sharp minimum at twice the plasmon frequency where two plasmon excitations become possible. Such a minimum is a typical sign of residual pole structure when going from a discrete bound state problem to a continuum problem such as the homogeneous electron gas. However this particular feature is not especially relevant for the Vignale-Kohn-Ullrich-Conti theory which is for slowly varying perturbations. The problem addressed by de Boeij, Kootstra, Berger, van Leeuwen, and Snijders [60] was to include the macroscopic exchange-correlation electric field in calculations of semiconductor excitation spectra. This is a nontrivial highly nonlocal contribution to the exchange-correlation functional associated with the development of surface charges and changes in the reaction field due to these charges when a polarizable solid is placed in an electric field. de Boeij *et al.* show how to derive an expression for the macroscopic exchange-correlation electric field in terms of the Vignale-Kohn-Ullrich-Conti theory and demonstrate how this improves absorption spectra for semiconductors, thus giving the first explicit example of a density-polarization functional.

It has been the author's contention that, at least for small molecules, the breakdown of the adiabatic approximation is rather minor for one-electron excitations compared to errors already present when common popular functionals are used in the adiabatic approximation. This contention has been largely confirmed by the general quality of excitation energies obtained by asymptotically-corrected functionals. Nevertheless it is known that, in contrast to common practical functionals which are relatively short ranged,

$$f_x^{\sigma,\tau}(\mathbf{r}, \mathbf{r}') \cong \delta(\mathbf{r} - \mathbf{r}') f_x^{\sigma,\tau}(\mathbf{r}, \mathbf{r}), \quad (\text{II.10})$$

the exact adiabatic exchange-correlation kernel is most likely rather long ranged. Thus Petersilka, Gossmann, and Gross[68] have shown that the kernel corresponding to Slater's model for the exchange-only potential, v_x , is

$$f_x^{\sigma,\tau}(\mathbf{r}, \mathbf{r}') = -\delta_{\sigma,\tau} \frac{|\gamma^\sigma(\mathbf{r}, \mathbf{r}')|^2}{\rho_\sigma(\mathbf{r})|\mathbf{r} - \mathbf{r}'|\rho_\sigma(\mathbf{r}')} . \quad (\text{II.11})$$

It might also contain particle-number derivative discontinuities [59]. Fortunately neglect of these effects in approximate adiabatic kernels does not seem to be a problem in many applications.

Applications where the overlocality of the kernel *does* seem to be a problem include finite segments of conducting polymers where the TDDFT method overestimates the dipole polarizability along the chain and this overestimate can be made as large as you like by simply making the segment longer and longer, [69] and improper scaling with respect to the number of K points in periodic calculations. [13] Since the hope is that DFT calculations should be useful for larger molecules than traditional *ab initio* calculations, it is disappointing to see cases where the error due to the functional seems to grow with the size of the molecule. Errors due to the overlocality of the kernel have also been seen as underestimated charge-transfer excitations in small molecules. [35, 52]

The solution at this point is not entirely clear but the area is under very active investigation. Certainly part of the solution for conducting polymers would seem to be the density-polarization functional of Boeij *et al.* [60], if it can be adopted for molecular solids and for isolated molecules. I have also already mentioned the Slater approximation for the kernel [68], and the charge-transfer correction [22, 52]. Recently, Burke, Petersilka, and Gross have combined these two ideas to suggest a hybrid method in which the parallel-spin component of the kernel is approximated by the Slater approximation while the TDLDA is retained for the antiparallel component of the kernel. [70] Since the basis for the charge-transfer correction was the idea that, at least under certain circumstances, the TDDFT and DFT Δ SCF methods should give the same excitation energies, I am excited by the recent demonstration of Gonze and Scheffler [71] that TDDFT with the TDA and 2LM gives the same answer as the Δ SCF method applied in the context of Görling-Levy adiabatic connection perturbation theory provided the exact exchange-only optimized potential theory is used within the Keldysh formalism of van Leeuwen [72].

III. CONCLUSION

The presence of TDDFT in most well-known quantum chemistry packages and its present popularity for applications, is an indication of the fact that TDDFT often works reasonably well in comparison with traditional *ab initio* methods, especially for larger molecules. It is in fact remarkable that a method which was virtually unknown in the quantum chemistry community as little as half a decade ago should have been so widely accepted. It has been the purpose of

this chapter to give a (necessarily biased) overview of present-day limitations of this still-young method and to suggest what directions should be pursued to improve functionals for practical applications of TDDFT. Together we have climbed the rungs of the ladders on Jacob’s jungle gym (Fig. 1). It is my hope that the reader will be able to take this information and be able to make somewhat wiser decisions about the choice of rungs appropriate for their accuracy requirements and computational resources.

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REFERENCES

- [1] Perdew, J.P.; Schmidt, K.; in: *Density Functional Theory and Its Applications to Materials*, edited by V.E. Van Doren, K. Van Alseoy, and P. Geerlings (American Institute of Physics, 2001). See also <http://www-chimie.ujf-grenoble.fr/PERSONNEL/LEDSS7/casida/CompChem/DFT.html>
- [2] <http://www.nobel.se/chemistry/laureates/1998/press.html> .
- [3] Car, R.; Parrinello, M *Phys. Rev. Lett.* **1985**, *55*, 2471.
- [4] Hohenberg, P.; Kohn, W.; *Phys. Rev.* **1964** *136*, B864.
- [5] Kohn, W.; Sham, L.J.; *Phys. Rev.* **1965**, *140*, A1133.
- [6] Casida, M.E.; in *Recent Advances in Density Functional Methods, Part I*, edited by D.P. Chong (World Scientific, Singapore, 1995), p. 155.
- [7] Jamorski, C.; Casida, M.E.; Salahub, D.R.; *J. Chem. Phys.* **1996** *104*, 5134.
- [8] Sundholm, D.; *Chem. Phys. Lett.* **1999**, *26*, 480.
- [9] Bauernschmitt, R.; Ahlrichs, R.; Hennrich, F.H.; Kappes, M.M.; *J. Am. Chem. Soc.* **1998**, *120*, 5052.
- [10] Champagne, B.; Perpète, E.A.; van Gisbergen, S.J.A; Baerends, E.J.; Snijders, J.G.; Soubra-Ghaoui, C.; Robins, K.A.; Kirtman, B.; *J. Chem. Phys.* **1998** *109*, 10489.
- [11] van Gisbergen, S.J.A.; Schipper, P.R.T.; Gritsenko, O.V.; Baerends, E.J.; Snijders, J.G.; Champagne, B.; Kirtman, B.; *Phys. Rev. Lett.* **1999**, *83*, 694.
- [12] Yabana K.; Bertsch, G.F.; *Int. J. Quant. Chem.* **1999** *75*, 55.
- [13] Hirata, S.; Head-Gordon, M.; Bartlett, R.J.; *J. Chem. Phys.* **1999** *111*, 10774.
- [14] van Gisbergen, S.J.A.; Groeneveld, J.A.; Rosa, A.; Snijders, J.G.; Baerends, E.J.; *J. Phys. Chem.* **1999**, *103*, 6835.

- [15] Boulet, P.; Chermette H.; Daul C.; Gilardoni, F.; Rogemond, F.; Weber, J.; Zuber, G.; *J. Phys. Chem. A* **2001**, *105*, 885.
- [16] Nguyen, K.A.; Day, P.N.; Pachter, R.; *J. Chem. Phys.* **1999**, *110*, 9135.
- [17] Lhiouhet, V.; Gutierrez, F.; Penaud, F.; Amouyal, E.; Daudey, J.-P.; Poteau, R.; Chouini-Lalanne, N.; Paillous, N.; *New Journal of Chemistry* **2000**, *24*, 403.
- [18] Casida, M.E.; Casida, K.C.; Salahub, D.R.; *Int. J. Quant. Chem.* **1998**, *70*, 933.
- [19] Spielfiedel, A.; Handy, N.C.; *Phys. Chem. Chem. Phys.* **1999**, *1*, 2401.
- [20] Ben-Nun, M.; Martínez, T.J.; *Chem. Phys.* **2000**, *257*, 237. (See footnote 2.)
- [21] Singh, R.; Deb, B.M.; *Physics Reports* **1999**, *311*, 47.
- [22] Casida, M.E.; Gutierrez, G.; Guan, J.; Gadea, F.-X.; Salahub, D.R.; Daudey, J.-P.; *J. Chem. Phys.* **2000**, *113*, 7062.
- [23] Gritsenko, O.V.; van Gisbergen, S.J.A.; Görling, A.; Baerends, E.J.; *J. Chem. Phys.* **2000**, *113*, 8478.
- [24] Van Caillie, C.; Amos, R.D.; *Chem. Phys. Lett.* **1999**, *308*, 249.
- [25] Van Caillie, C.; Amos, R.D.; *Chem. Phys. Lett.* **2000**, *317*, 159.
- [26] Frank, I.; Hutter, J.; Marx, D.; Parrinello, M.; *J. Chem. Phys.* **1998**, *108*, 4060.
- [27] Dotsinis, N.L.; Sprik, M.; *Chem. Phys. Lett.* **2000**, *330*, 563.
- [28] Röhrig, U.; Laio, A.; VandeVondele, J.; Hullo, J.; Röthlisberger, U; *to be published*.
- [29] Bartlett, R.J.; in *Chemistry for the 21st Century*, edited by E. Keinan and I. Schechter (Wiley-VCH, Weinheim, 2000), p. 271.
- [30] Koch, W.; Holthausen, M.C.; *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, New York, 2000),
- [31] Hamprecht, F.A.; Cohen, A.J.; Tozer, D.J.; Handy, N.C.; *J. Chem. Phys.* **1998**, *109*, 6264.
- [32] van Leeuwen, R.; Baerends, E.J.; *Phys. Rev. A* **1994**, *49*, 2421.
- [33] Gritsenko, O.V.; Schipper, P.R.T.; Baerends, E.J.; *Chem. Phys. Lett.* **1999**, *302*, 199.
- [34] Tozer, D.J.; Handy, N.C.; *J. Chem. Phys.* **1998**, *108*, 2545.
- [35] Tozer, D.J.; Amos, R.D.; Handy, N.C.; Roos, B.O.; Serrano-Andrés, L.; *Mol. Phys.* **1999**, *97*, 859.
- [36] Casida, M.E.; Salahub, D.R.; *J. Chem. Phys.* **2000**, *113*, 8918.
- [37] Grüning, M.; Gritsenko, O.V.; van Gisbergen, S.J.A.; Baerends, E.J.; *J. Chem. Phys.* **2001**, *114*, 652.
- [38] Ziegler, T.; Rauk, A.; Baerends, E.J.; *Theor. Chim. Acta* **1977**, *43*, 877.
- [39] Daul, C.; *Int. J. Quant. Chem.* **1994**, *52*, 867.
- [40] Peuckert, V.; *J. Chem. Phys. C* **1978**, *11*, 4945.
- [41] Chakravarty, S.; Fogel, M.B.; Kohn, W.; *Phys. Rev. Lett.* **1979**, *43*, 775.
- [42] Bartolotti, L.J.; *Phys. Rev. A* **1981**, *24*, 1661.
- [43] Bartolotti, L.J.; *Phys. Rev. A* **1982**, *26*, 2243.
- [44] Deb, B.H.; Ghosh, S.K.; *J. Chem. Phys.* **1982**, *77*, 342.
- [45] Runge, E.; Gross, E.K.U.; *Phys. Rev. Lett.* **1984**, *52*, 997.
- [46] Kohl, H.; Dreizler, R.M.; *Phys. Rev. Lett.* **1986**, *56*, 997.
- [47] Mearns, D.; Kohn, W.; *Phys. Rev. A* **1987**, *35*, 4796.
- [48] van Leeuwen, R.; *Phys. Rev. Lett.* **1998**, *80*, 1280.
- [49] Gross, E.K.U.; Kohn, W.; *Adv. Quant. Chem.* **1990**, *21*, 255.
- [50] Gross, E.K.U.; Ullrich, C.A.; Gossmann, U.J.; in *Density Functional Theory*, edited by E.K.U. Gross and R.M. Dreizler, NATO ASI Series (Plenum, New York, 1994), p. 149.
- [51] Gross, E.K.U.; Dobson, J.F.; Petersilka, M.; in *Density Functional Theory II*, Vol. 181 of *Topics in Current Chemistry*, edited by R.F. Nalewajski (Springer, Berlin, 1996), p. 149.
- [52] M.E. Casida, in the *On-line Workshop Proceedings of the Joint ITP/INT Workshop on Time-Dependent Density Functional Theory*, 15-17 April 1999, Institute for Theoretical Physics, University of California at Santa Barbara: http://www.itp.ucsb.edu/online/tddft_c99/
- [53] Bauernschmitt, R.; Ahlrichs, R.; *J. Chem. Phys.* **1996**, *104*, 9047.
- [54] Casida, M.E.; Jamorski, C.; Casida, K.C.; Salahub, D.R.; *J. Chem. Phys.* **1998**, *108*, 4439.
- [55] Hamel, S.; Casida, M.E.; Salahub, D.R.; *J. Chem. Phys.* submitted.
- [56] Sharp, R.T.; Horton, G.K.; *Phys. Rev.* **1953**, *90*, 317.
- [57] Talman, J.D.; Shadwick, W.F.; *Phys. Rev. A* **1976**, *14*, 36.
- [58] Hirata, S.; Ivanov, S.; Grabowski, I.; Bartlett, R.J.; Burke, K.; Talman, J.D.; *J. Chem. Phys.* **2001**, *115*, 1635.

- [59] Casida, M.E.; in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J.M. Seminario (Elsevier, Amsterdam, 1996), p. 391.
- [60] de Boeij, P.L.; Kootstra, F.; Berger, J.A.; van Leeuwen, R.; Snijders, J.G.; *J. Chem. Phys.* **2001**, *115*, 1995.
- [61] Gross, E.K.U.; Kohn, W.; *Phys. Rev. Lett.* **1985**, *55*, 2850.
- [62] Dobson, J.F.; *Phys. Rev. Lett.* **1994**, *73*, 2244.
- [63] Vignale, G.; *Phys. Rev. Lett.* **1995**, *74*, 3233.
- [64] Vignale, G.; Kohn, W.; *Phys. Rev. Lett.* **1996**, *77*, 2037.
- [65] Vignale, G.; Ullrich, C.A.; Conti, S.; *Phys. Rev. Lett.* **1997**, *79*, 4878.
- [66] Dobson, J.F.; Büchner, M.J.; Gross, E.K.U.; *Phys. Rev. Lett.* **1997**, *79*, 1905.
- [67] Nifosì, R.; Conti, S.; Tosi, P.; *Phys. Rev. B*, **1998**, *58*, 12758.
- [68] Petersilka, M.; Gossmann, U.J.; Gross, E.K.U.; *Phys. Rev. Lett.* **1996** *76*, 1212.
- [69] Champagne, B.; *et al.*; *J. Chem. Phys.* **1998**, *109*, 10489.
- [70] Burke, K.; Petersilka, M.; and Gross, E.K.U.; in *Recent Advances in Density Functional Methods, Vol III*, edited by P. Fantucci and A. Bencini (World Scientific Press, 2000).
- [71] Gonze, X.; Scheffler, M.; *Phys. Rev. Lett.* **1999** *82*, 4416.
- [72] van Leeuwen, R.; *Phys. Rev. Lett.* **1998** *80*, 1280.