Over the last years the theoretical description of optical properties of complex many-electron systems, from molecules, to nanostructures and extended systems, has re-flourished due to the efficient implementation of time-dependent density-functional theory (TDDFT) \[1\] \[2\]. The good performance shown by the adiabatic local density approximation (ALDA) for many finite systems has limited the development of exchange-correlation (xc) functionals with a more elaborate time-dependence, which is clearly in its infancy compared to static DFT. However recently many important deficiencies, especially of the adiabatic approximation, have been identified \[3\] \[4\] \[5\] \[6\] \[7\] \[8\].

Ultrafast time-resolved optical spectroscopy has revealed new classes of physical, chemical, and biological reactions, in which directed, deterministic motions of atoms have a key role. The advent of free electron lasers with attosecond resolution increases the capabilities of present femtosecond pump-probe experiments, allowing for a study of the dynamics of non-equilibrium electronic systems in real time. In addition, systems of all sizes can be investigated, from the atomic scale to the most extended molecules (e.g. DNA, proteins and their complexes) and solids. Despite those tremendous experimental advances, the theoretical description of a real molecular subject to ultrafast, intense, and/or high-frequency lasers is still in a fledgling state. Several problems need to be addressed, ranging from the non-perturbative nature of the physical processes involved to the simultaneous description of the (interacting) electronic and nuclear degrees of freedom. Therefore, it is of paramount relevance to have a theoretical framework which allows for a non-perturbative description of electrons, and at the same time is able to tackle electron dynamics in the excited-state. TDDFT seems to be the suitable framework to move the realm of density-functional methods beyond the linear regime to describe the aforementioned processes. One important advantage is the combined electron and ion dynamics provided by TDDFT \[9\].

Many physical processes rely on the knowledge of non-linear response functions. Therefore, it is very timely to provide a systematic study addressing the performance of present functionals in the non-linear regime. To assess the quality of a functional we need to have appropriate data for comparison. Obtaining accurate experimental data in the non-linear regime can be very difficult for real systems, due to various limitations, e.g. solvent effects or additional approximations going into the interpretation of the collected data \[10\] \[11\]. These problems can be avoided by using exactly solvable models which then allow for a direct comparison between the exact spectrum and an approximate one. Unfortunately, an exact propagation of even small three-dimensional systems is computationally very demanding, and needs further simplification. One possibility is the reduction of dimensionality,
i.e. the use of one-dimensional (1D) models, where the exact diagonalization is feasible as long as the number of electrons is sufficiently small. In the present paper we work with systems of interacting electrons in 1D. Having the exact solution allows us to test orbital dependent functionals such as exact exchange (EXX) which can be easily transferred to different dimensions. A local density approximation (LDA) is achieved, as in the 3D case, by quantum Monte-Carlo (QMC) studies of the homogeneous reference, and parametrizing the corresponding correlation energy.

The present work, besides adding fundamental information concerning the relevance of spatial and time non-locality in the xc functional, also provides a proper LDA parametrization for electrons interacting via the soft-Coulomb interaction in 1D systems. This model description is widely used in the context of high-intensity lasers, where above-threshold ionization and high-harmonic generation play an important role [15–18]. Also, 1D two-electron systems are employed to gain insight into exact properties of the xc potential and kernel in static and time-dependent density functional theory, since these systems can easily be solved exactly [19–21].

The 1D Hamiltonian for \( N \) particles moving in a general external potential \( v_{\text{ext}} \) reads

\[
H = \sum_{j=1}^{N} \left[ -\frac{1}{2} \frac{\partial^2}{\partial x_j^2} + v_{\text{ext}}(x_j) \right] + \frac{1}{2} \sum_{j,k=1}^{N} \delta_{jk} v_{\text{int}}(x_j, x_k),
\]

where \( v_{\text{int}} \) describes the electron-electron interaction. In order to avoid the singularity of the Coulomb interaction we employ the soft-Coulomb potential

\[
v_{\text{soft-Coulomb}}(x_1, x_2) = \frac{q_1 q_2}{\sqrt{a^2 + (x_1 - x_2)^2}},
\]

instead. Here, \( q_1 \) and \( q_2 \) describe the charges of the particles while \( a \) is the usual softening parameter (atomic units \( e = m = \hbar = 1 \) are used throughout this paper). Unless stated explicitly, we use \( a = 1 \) for all our calculations. Mathematically, it is straightforward to show that the Hamiltonian (1) is equivalent to a single particle in \( N \) dimensions, moving in an external potential consisting of all the contributions from \( v_{\text{ext}} \) and \( v_{\text{int}} \). The corresponding Schrödinger equation can, hence, be solved by any code which is able to treat non-interacting particles in the correct number of dimensions in an arbitrary external potential. Due to the Hamiltonian being symmetric under particle interchange, \( x_j \leftrightarrow x_k \), the solutions of the Schrödinger equation can be chosen as symmetric or antisymmetric under such an exchange. For the simplest case of two interacting electrons both the symmetric and antisymmetric solutions are valid, corresponding to the singlet and triplet spin configurations, respectively. However, for more than two electrons one needs to separately ensure that the spatial wave function is a solution to the \( N \)-electron problem. For example, a totally symmetric spatial wave function is a correct solution for a single particle in \( N \) dimensions, however, for \( N > 2 \) there is no corresponding spin function such that the total wave function has the required antisymmetry to be a solution of the \( N \) fermion problem in 1D. We solve this problem by symmetrizing the solutions according to all possible fermionic Young diagrams for the given particle number \( N \). The solution of higher dimensional problems within these symmetry restrictions has been implemented into the OCTOPUS computer program [23, 24]. Usually, the lowest energy solution is found to be purely symmetric and is discarded for \( N > 2 \). With increasing number of electrons we also observe an increasing number of states which do not satisfy the fermionic symmetry requirements.

As a result of reducing the number of dimensions, we need to use an appropriate functional for performing the DFT calculations. While any orbital functional can easily be transferred between dimensions, those functionals based on specific systems need to be recalculated. This affects the most common functional, i.e. the local density approximation, available only for the normal Coulomb interaction in two and three dimensions [25, 26], an effective Coulomb interaction of a harmonically confined wire [27, 28], and some other ad-hoc 1D models [28]. In this work, we present and use a parametrization of the 1D LDA obtained from quantum Monte-Carlo simulations, which are exact in 1D, using the soft-Coulomb interaction in Eq. (2). We assess the quality of the approximation in calculating ground-state properties as well as the linear response for various 1D model systems. We then proceed to calculate the nonlinear response and compare the exact one with the ALDA and adiabatic exact-exchange (AEXX) spectra.

The correlation energy of the LDA is parametrized in terms of \( r_s \) and the spin polarization \( \zeta = (N_\uparrow - N_\downarrow)/N \) in the form

\[
\epsilon_c(r_s, \zeta) = \frac{\epsilon_c(r_s, \zeta = 0) + \zeta^2 [\epsilon_c(r_s, \zeta = 1) - \epsilon_c(r_s, \zeta = 0)]}{2}.
\]

with

\[
\epsilon_c(r_s, \zeta = 0, 1) = -\frac{1}{2} \frac{r_s + Er_s^2}{A + Br_s + Cr_s^2 + Dr_s^3} \ln(1 + \alpha r_s + \beta r_s^m),
\]

which proved to be very accurate in the parametrization for other 1D systems with a different long-range interaction [27]. Note that the additional factor of 1/2 is due the use of Hartree atomic units, as everywhere else in the paper. To obtain the exact high-density result, known from the random phase approximation [28], i.e.

\[
\epsilon_0(r_s \rightarrow 0, \zeta = 0) = -4/(\pi^2 a^2) r_s^2,
\]

\[
\epsilon_0(r_s \rightarrow 0, \zeta = 1) = -1/(2\pi^2 a^2) r_s^2
\]
TABLE I: Values of the LDA correlation energy parametrization in Eq. [4] For the most widely used case, i.e. \( \alpha = 1 \), the parametrization is reported for both unpolarized \( (\zeta = 0) \) and fully polarized \( (\zeta = 1) \) systems. The error on the last digits is given in parenthesis, while the average error (in Hartree) in the full density range is given in the last row.

| \( \alpha = 1.0 \) | \( \zeta = 0 \) | \( \zeta = 1 \) | \( \alpha = 0.5 \) | \( \zeta = 0 \) |
|----------------|----------------|----------------|----------------|----------------|
| \( A \) | 18.40(29) | 5.24(79) | 7.40(18) |
| \( B \) | 0.0 | 0.0 | 1.120(119) |
| \( C \) | 7.501(39) | 1.568(230) | 1.890(63) |
| \( D \) | 0.10185(5) | 0.0320(74) | 0.0250(23) |
| \( \alpha \) | 1.511(24) | 0.038(82) | 2.431(62) |
| \( \beta \) | 0.258(6) | 1.56(131) \cdot 10^{-5} | 0.0142(25) |
| \( m \) | 4.424(25) | 2.958(99) | 2.922(83) |
| av. error | 6.7 \cdot 10^{-5} | 3.3 \cdot 10^{-5} | 7.7 \cdot 10^{-4} |

TABLE II: Total energies and ionization potentials for one-dimensional atoms and ions from exact and (spin-)LDA calculations as well as the eigenvalues of the highest occupied Kohn-Sham orbital. All numbers are given in Hartree.

| System | \( E_{\text{total}} \) | \( E_{\text{HOMO}} \) | IP |
|-------|----------------|----------------|-----|
| \( \text{H} \) | -0.67 | -0.60 | -0.65 |
| \( \text{He} \) | -2.24 | -2.20 |
| \( \text{Li} \) | -1.41 | -1.46 | -1.48 |
| \( \text{Be} \) | -6.78 | -6.76 |
| \( \text{He}^+ \) | -1.48 | -1.41 | -1.45 |
| \( \text{Li}^+ \) | -3.90 | -3.85 |
| \( \text{Be}^+ \) | -6.45 | -6.39 | -6.41 |
| \( \text{Li}^{2+} \) | -2.34 | -2.25 | -2.30 |
| \( \text{Be}^{2+} \) | -5.62 | -5.56 |
| \( \text{Be}^{3+} \) | -3.21 | -3.13 | -3.18 |

As a first test, we calculated the ground-state energies of small atomic systems, for example, a 1D helium atom with \( q = 2 \) in Eq. [3] and two electrons which interact via the soft Coulomb interaction. The ground state energies and ionization potentials from the exact and unpolarized LDA calculations are given in Tab. [II]. We include all possible systems with one, two, three and four electrons in our test. For open-shell systems, we additionally performed a spin-DFT (SLDA) calculation, where the xc energy is spin dependent according to Eq. [3]. All atomic calculations were performed in a box ranging from -8 to 8 bohr with a spacing of 0.2 bohr, which ensures the total energy to be converged to the accuracy stated in the table.

As we can see, the LDA total energies for the neutral and positively charged systems agree very well with the exact results. As expected, the spin-resolved calculations further improve the agreement for the open-shell systems. As a result, the ionization potentials, calculated as the difference of the total energies of the \( N \) and the \( N - 1 \) electron systems, from the (S)LDA and the exact calculations agree almost perfectly. The largest Kohn-Sham eigenvalue \( \epsilon_{\text{HOMO}} \) only partially accounts for the total ionization potential, i.e. the 1D LDA violates this known property of the exact functional. The good agreement for the positively charged systems is not reproduced for negatively charged ones. For the small systems investigated here, LDA does not bind an extra electron while the exact calculation shows that the negatively charged systems are indeed stable giving total energies of \(-0.73 \text{ Ha} \), \(-2.35 \text{ Ha} \), and \(-4.17 \text{ Ha} \) for \( \text{H}^- \), \( \text{He}^- \), and \( \text{Li}^- \), respectively. A comparison with the total energies of the neutral systems shows that in the exact calculation the additional electron is only very lightly bound in 1D. It is no surprise that the LDA, with its usual wrong asymptotic behavior of the exchange-correlation potential, does not yield stable negatively charged ions.

As a second test of the new functional we calculate the dissociation curve of the 1D hydrogen molecule. For these calculations we increased the size of the simulation box to range from -20 to 20 bohr in order to achieve convergence also for the stretched molecule. Fig. [II] shows the
binding energy per atom as a function of the distance between the two ions. As one can see, the known pathology of 3D LDA is reproduced also in 1D. The singlet state yields a good description around the equilibrium distance of 1.6 bohr with the binding energy being slightly overestimated by LDA. However, the bond breaking is not described correctly due to the strong static correlation at large distances. The LDA calculation for the triplet state yields very good agreement over the whole range of distances corroborating the general experience of LDA performing better for more polarized systems.

After having shown that the 1D LDA behaves very much like its 3D counterpart for ground-state calculations, we turn our attention to TDDFT where we use it as an adiabatic approximation to the exact time-dependent exchange-correlation potential. The propagations were performed in a box ranging from -150 to 150 bohr with absorbing boundary conditions [23] and a grid spacing of 0.2 bohr for a total propagation time of $10^3$ a.u.

In Fig. 2 we compare the spectra calculated in a linear and non-linear regime from the exact and the 1D LDA calculation.

![Figure 2: Linear (top) and non-linear (bottom) spectra of Be$^{2+}$ comparing the exact and the 1D LDA calculation. The inset in the bottom figure shows a zoom into the region from 2.7 to 3.0 Ha.](image)

| $\omega_1$ | $\omega_2$ | $\omega_3$ | $\omega_4$ | $\omega_5$ | $\omega_6$ | $\omega_7$ | $\Omega_1$ | $\Omega_2$ | $\Omega_3$ |
|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| LDA        | 1.10       | 1.74       | 1.90       | 1.96       | 2.00       | -          | -          | 0.22       | 0.40       |
| EXX        | 1.13       | 1.82       | 2.08       | 2.20       | 2.27       | 2.30       | 2.32       | 0.26       | 0.43       | 0.52       |
| exact      | 1.12       | 1.81       | 2.08       | 2.20       | 2.27       | 2.29       | 2.32       | 0.28       | 0.42       | 0.54       |

TABLE III: Excitation energies from linear and non-linear response of the 1D Be$^{2+}$ atom corresponding to the spectra in Fig. 2. Excitations from linear response are denoted as $\omega$ while those from the non-linear spectrum are denoted with $\Omega$. All numbers are given in Hartree.
of resonance \(\mathbb{E}_0\), i.e. the decay of an excited state into continuum states. It is missing from both approximate spectra due to the double-excitation character of the involved excited state. Double excitations can only be described in TDDFT if a frequency-dependent xc kernel is employed. Any adiabatic approximation, however, leads to a frequency independent kernel. Hence, double excitations, as well as any resulting features, are missing from both the ALDA and the AEXX calculations. Apart from the well-known shortcomings of not including double-excitations and not giving the correct Rydberg series, the 1D ALDA reproduces both the linear and the non-linear exact spectra quite well.

We have introduced a one-dimensional LDA suitable for the description of systems interacting via the commonly used soft-Coulomb interaction. We have shown that the one-dimensional functional is of the same quality as its three-dimensional counterpart in the calculation of ground-state energies of atomic systems and the dissociation of small molecules. Also, the linear spectra show the same quality known from 3D calculations with low energy excitations being well described while Rydberg and double excitations are missing. Generally, for the 1D LDA one can expect the same success and failure in applications that are known from 3D calculations, i.e. the quality of the LDA results appears to be independent of the dimensionality. We emphasize that the 1D LDA yields a good description not only in linear response but also in the non-linear case. Consequently, one can expect 3D LDA calculations to perform well for the calculation of non-linear response, where the experimental data is often difficult to interpret.

The reduced dimensionality of the model systems treated in this work allows for a direct solution of the interacting problem for small number of particles. The comparison between the DFT and an exact calculation allows for an assessment of the quality of approximations beyond what is possible in three-dimensional systems. One-dimensional model systems can provide useful insight which hopefully will allow for the construction of new functionals in the future.

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[1] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).
[2] Time-Dependent Density Functional Theory, Vol. 706 of Lecture Notes in Physics, edited by M. A. L. Marques et al. (Springer Berlin / Heidelberg, 2006).
[3] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002).
[4] N. T. Maitra, K. Burke, and C. Woodward, Phys. Rev. Lett. 89, 023002 (2002).
[5] N. T. Maitra, F. Zhang, R. Cave, and K. Burke, J. Chem. Phys. 120, 5932 (2004).
[6] A. Dreuw and M. Head-Gordon, J. Am. Chem. Soc. 126, 4007 (2004).
[7] N. Maitra, J. Chem. Phys. 122, 234104 (2005).
[8] K. Burke, J. Wierschnik, and E. K. U. Gross, J. Chem. Phys. 123, 062206 (2005).
[9] D. Varsano, A. Marini, and A. Rubio, Phys. Rev. Lett. 101, 133002 (2008).
[10] TDDFT for Molecules and Molecular Solids, edited by M. Casida, H. Chermette, and D. Jacquemin (Special Issue in Journal of Molecular Structure: THEOCHEM, vol. 914, Issues 1-3 2009).
[11] L. Goerigk, J. Moellmann, and S. Grimme, Phys. Chem. Chem. Phys. 11, 4611 (2009).
[12] O. Gritsenko and E. Baerends, Phys. Chem. Chem. Phys. 11, 4640 (2009).
[13] M. Stahelin et al., J. Chem. Phys. 98, 5595 (1993).
[14] P. Kaatz, E. Donley, and D. Shelton, J. Chem. Phys. 108, 849 (1998).
[15] J. Javanainen, J. Eberly, and Q. Su, Phys. Rev. A 38, 3430 (1988).
[16] J. Eberly, Phys. Rev. A 42, 5750 (1990).
[17] M. Lein, E. K. U. Gross, and V. Engel, Phys. Rev. Lett. 85, 4707 (2000).
[18] M. Lein, Phys. Rev. A 72, 053816 (2005).
[19] M. Thiele, E. K. U. Gross, and S. Kümmer, Phys. Rev. Lett. 100, 153004 (2008).
[20] D. G. Tempel, T. J. Martinez, and N. T. Maitra, J. Chem. Theory and Computation 5, 770 (2009).
[21] N. Helbig, I. Tokatly, and A. Rubio, J. Chem. Phys. 131, 224105 (2009).
[22] L.D. Landau and E.M. Lifschitz, Quantum Mechanics (Butterworth-Heinemann, Oxford, 1977).
[23] M. A. L. Marques, A. Castro, G. F. Bertsch, and A. Rubio, Comp. Phys. Comm. 151, 60 (2003).
[24] A. Castro et al., Phys. Stat. Sol. (b) 243, 2465 (2006).
[25] C. Attaccalite, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. Lett. 88, 256601 (2002).
[26] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[27] M. Casula, S. Sorella, and G. Senatore, Phys. Rev. B 74, 245427 (2006).
[28] M. Chisholm, M. Casula, G. Sorella, and G. Senatore, Phys. Rev. B 74, 245427 (2006).
[29] L. Shulenburger, M. Casula, G. Senatore, and R. Martin, J. Phys. A: Math. Theor. 42, 214021 (2009).
[30] G. Xianlong et al., Phys. Rev. B 73, 165120 (2006).
[31] G. Xianlong, M. Polini, R. Asgari, and M. P. Tosi, Phys. Rev. A 73, 033609 (2006).
[32] G. Xianlong and R. Asgari, Phys. Rev. A 77, 033604 (2008).
[33] C.-O. Almbladh and U. von Barth, Phys. Rev. B 31, 3231 (1985).
[34] U. Fano, Phys. Rev. 124, 1866 (1961).
[35] U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).