# Nonlinear response in Density Functional Theory: LDA versus exact


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## Abstract


*We present a local density approximation (LDA) for onedimensional systems interacting via softCoulomb interaction based on Monte Carlo calculations. Results for the groundstate energies and ionization potentials of finite systems show excellent agreement with the exact calculations. Similarly to what is known from three-dimensional LDA, the electron affinities are too small with several systems not binding an additional electron contrary to the exact result. We conclude that the one-dimensional LDA is of the same quality as its threedimensional counterpart which permits us to draw conclusions about threedimensional LDA, when comparison to experiments are difficult and exact theoretical results not available. The linear and nonlinear timedependent responses of onedimensional model systems using LDA, exact exchange, and the exact solution are investigated and show very good agreement in both cases except for the well known problem of missing double excitations. Consequently, three-dimensional LDA is expected to be of good quality beyond linear response. In addition, the onedimensional LDA should prove useful in modeling the interaction of atoms with strong laser fields where this specific onedimensional model is often used.*


## 1D Model systems

- One-dimensional models describe for example systems in strong laser fields
- 1D model systems are ideally suited for theoretical development
- Hamiltonian for $N$ particles in a general external potential $v_{ext}$ in one dimension

$$H = \sum_{j=1}^{N} -\frac{d^2}{dx_j^2} + v_{ext}(x_j) + \frac{1}{2}\sum_{\substack{j,k=1 \\ j\neq k}}^{N} v_{int}(x_j, x_k), \quad (1)$$

with the soft-Coulomb interaction

$$v_{int}(x_1, x_2) = \frac{q_1 q_2}{\sqrt{a^2 + (x_1 - x_2)^2}} \quad (2)$$

Unless stated explicitly, we use $a = 1$ for all our calculations.

- The Hamiltonian (1) is equivalent to a single particle in $N$ dimensions; the corresponding Schrödinger equation can be solved exactly
- Symmetry of the Hamiltonian ensures that solutions are either symmetric or antisymmetric under particle exchange
- Bosonic solutions need to be removed by projecting on fermionic Young diagrams
- Implemented in the `OCTOPUS` computer program [1, 2]

## 1D LDA

- LDA is based on Monte-Carlo calculations for 1D homogeneous electron gas
- Parametrization of the correlation energy [3, 4]

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

- Exact high density result known from RPA

$$\epsilon_c(r_s \to 0) = -\frac{\alpha}{A} r_s^2 \quad (3)$$

$\Rightarrow \alpha/A = 8/(\pi^4 a^2)$.

- 7 independent parameters remain, for $a = 1$

| | |
|---|---|
| $A = 18.40(29)$ | $\alpha = 1.511(24)$ |
| $B = 0$ | $\beta = 0.258(6)$ |
| $C = 7.501(39)$ | $m = 4.424(25)$ |
| $D = 0.10185(5)$ | |
| $E = 0.012827(10)$ | |

- Overall error in the correlation energy of $6.7 \cdot 10^{-5}$

## Total energies and ionization potentials

- LDA total energies for neutral and positively charged systems agree very well with exact results
- No binding of additional electron in LDA calculation
- HOMO energies smaller than ionization potential

| | $E_{\text{total}}$ | | | IP | | |
|---|---|---|---|---|---|---|
| | Exact | LDA | SLDA | Exact | (S)LDA | $\epsilon^{\text{SLDA}}_{\text{HOMO}}$ |
| H | -0.67 | -0.60 | -0.68 | 0.67 | 0.68 | 0.48 |
| He | -2.24 | -2.20 | | 0.75 | 0.72 | 0.51 |
| Li | -4.21 | -4.16 | -4.21 | 0.31 | 0.36 | 0.26 |
| Be | -6.78 | -6.76 | | 0.33 | 0.33 | 0.20 |
| $He^+$ | -1.48 | -1.41 | -1.48 | 1.48 | 1.48 | 1.22 |
| $Li^+$ | -3.90 | -3.85 | | 1.56 | 1.52 | 1.26 |
| $Be^+$ | -6.45 | -6.39 | -6.43 | 0.89 | 0.87 | 0.69 |
| $Li^{2+}$ | -2.34 | -2.25 | -2.33 | 2.34 | 2.33 | 2.04 |
| $Be^{2+}$ | -5.62 | -5.56 | | 2.41 | 2.36 | 2.08 |
| $Be^{3+}$ | -3.21 | -3.13 | -3.20 | 3.21 | 3.20 | 2.89 |

**Table 1:** *Total energies and ionization potentials for one-dimensional atoms and ions from exact and (spin-)LDA calculations as well as the eigenvalue of the highest occupied Kohn-Sham orbital. All numbers are given in Hartree.*

Quality of 1D LDA very similar to 3D for ground-state calculations

## Linear response

- Use 1D LDA in an adiabatic approximation in TDDFT
- Apply small kick (0.001) at $t = 0$ and evolve the system
- Compare exact and ALDA spectra

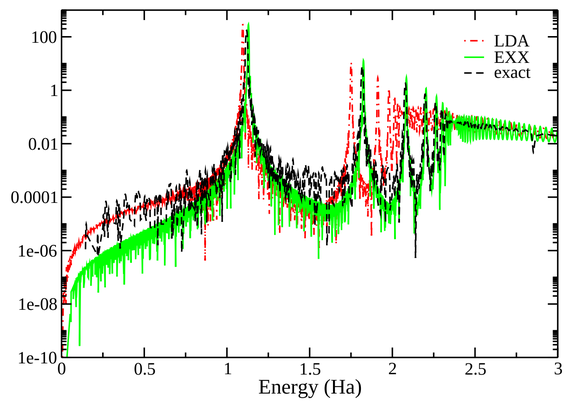



**Fig. 1:** *Linear spectrum of $Be^{2+}$ comparing the exact and the 1D LDA calculation. Exact exchange (EXX) included for further comparison.*

- First five LDA peaks agree well with exact ones
- Agreement better for lower lying excitations
- Onset of continuum at too low energies, no Rydberg series in LDA
- Exact exchange shows slightly better agreement, especially for Rydberg states
- Dip at 2.8 Ha due to Fano resonance [5] involving a doubly-excited state

Quality of 1D LDA identical to 3D within linear response regime, double excitations are missing

## Nonlinear response

- Use 1D LDA in an adiabatic approximation in TDDFT
- Increase strength of kick to 0.1

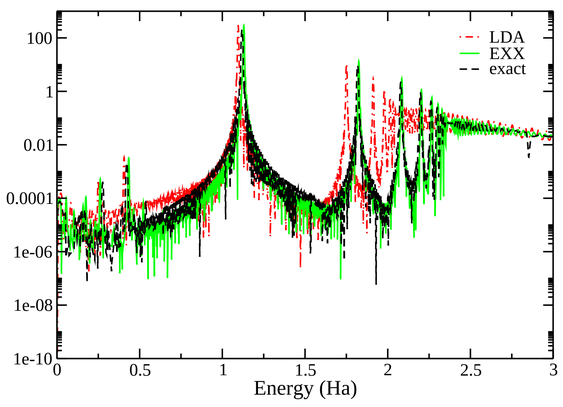
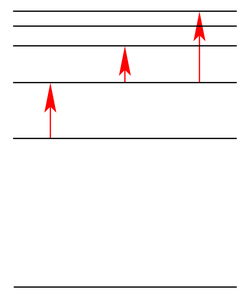



**Fig. 2:** *Nonlinear spectrum of $Be^{2+}$ comparing the exact and the 1D LDA calculation. Exact exchange (EXX) included for further comparison.*

- Three additional peaks in exact spectrum from third order response
- Second order response is zero due to symmetry of the system
- LDA shows only two peaks, again due to onset of continuum at too low energies
- $\omega = 0.28$ Ha corresponds to a transition from second to third excited state
- $\omega = 0.42$ Ha and $\omega = 0.54$ Ha, correspond to the transitions from first to second and second to fifth excited state, respectively
- Both LDA and EXX yield good descriptions of low lying excitations



## Conclusions

- One-dimensional LDA reproduces ground-state properties of 1D systems with the same accuracy as its 3D counterpart does for 3D systems
- Linear response LDA spectra agree well with exact excitations apart from Rydberg states and double excitations
- Quality of ground-state and linear response calculations similar in one and three dimensions
- Nonlinear response LDA spectra agree well with exact spectra for low lying excitations

Local density approximation is expected to be valid in TDDFT beyond the linear regime independent of the dimensionality of the system

- Experimental results for strong laser fields can be difficult to interpret
- Local density approximation can be trusted beyond the linear regime

## References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