Time-dependent density-functional and reduced density-matrix methods for few electrons: Exact versus adiabatic approximations

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ABSTRACT

To address the impact of electron correlations in the linear and non-linear response regimes of interacting many-electron systems exposed to time-dependent external fields, we study one-dimensional (1D) systems where the interacting problem is solved exactly by exploiting the mapping of the 1D N-electron problem onto an N-dimensional single electron problem. We analyze the performance of the recently derived 1D local density approximation as well as the exact-exchange orbital functional for those systems. We show that the interaction with an external resonant laser field shows Rabi oscillations which are detuned due to the lack of memory in adiabatic approximations. To investigate situations where static correlations play a role, we consider the time-evolution of the natural occupation numbers associated to the reduced one-body density matrix. Those studies shed light on the non-locality and time-dependence of the exchange and correlation functionals in time-dependent density and density-matrix functional theories.

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1. Introduction

Since its invention in 1984 time-dependent density-functional theory (TDDFT) has become one of the major tools for describing time-dependent phenomena of electronic systems [1,2]. Despite its success, several important questions remain open. A prominent example are double excitations [3], which cannot be described with adiabatic approximations to the exchange-correlation (xc) kernel [4]. Other examples include the description of memory [5], charge-transfer excitations [6], Rabi oscillations [7], and population control [8,9]. Also, the construction of functionals for certain observables can be problematic, like e.g. double-ionization in strong laser fields where one strategy rests on expressing the pair-correlation function as a functional of the time-dependent density [10].

In many cases, there is little knowledge about how the dynamics of the many-body system interacting with an arbitrary external time-dependent field is mapped onto the non-interacting (time-dependent) Kohn–Sham system. Here, one-dimensional systems can provide insight since these systems can be exactly diagonalized and subsequently propagated in time for a small number of electrons. We provide insight into the limitations of adiabatic functionals, especially for describing non-linear electron dynamics exemplified by the case of Rabi oscillations.

This article is organized as follows, we first highlight the exact mapping of a many-electron system onto an N-dimensional one-electron problem and the selection of proper fermionic solutions. Then, we discuss the recently developed one-dimensional local density approximation (LDA) and its performance for calculating linear and non-linear response. We use the LDA as well as exact exchange (EXX) to investigate the description of double excitations and Rabi oscillations with adiabatic approximations. We then change from TDDFT to reduced density-matrix functional theory, where we discuss under which conditions adiabatic approximations provide a valid description. We conclude the paper with a short summary and perspectives.

2. One-dimensional model systems

The Hamiltonian for N electrons moving in a general, possibly time dependent, external potential v_{ext} in one spatial dimension reads

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$$H = \sum_{j=1}^{N} \left[-\frac{d^2}{2dx_j^2} + v_{\text{ext}}(x_j, t) \right] + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^{N} v_{\text{int}}(x_j, x_k), \tag{1}$$

where v_{int} describes the electron–electron interaction (atomic units $e = m = \hbar = 1$ are used throughout this paper). In one spatial dimension the singularity of the ordinary Coulomb interaction prevents electrons from passing the position of the singularity, both in the attractive and repulsive case. In order to avoid this unphysical behavior of the full Coulomb interaction we employ the so called soft-Coulomb interaction

$$v_{\text{soft-C}}(x_1, x_2) = \frac{q_1 q_2}{\sqrt{a^2 + (x_1 - x_2)^2}} \tag{2}$$

instead [11]. Here, q_1 and q_2 describe the charges of the particles while a is the usual softening parameter. We use $a = 1$ for all our calculations. Mathematically, it is straightforward to show that the Hamiltonian (1) is equivalent to a Hamiltonian for a single particle in N dimensions moving in an external potential

$$v_{\text{Ndim}}(x_1 \ldots x_N) = \sum_{j=1}^{N} v_{\text{ext}}(x_j) + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^{N} v_{\text{int}}(x_j, x_k) \tag{3}$$

consisting of all the contributions from v_{ext} and v_{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 classified according to irreducible representations of the permutation group. 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. 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 particle problem in 1D. We solve this problem by symmetrizing the solutions according to all possible fermionic Young diagrams for the given particle number N [12]. Fig. 1 shows all possible standard Young diagrams for the spatial part of the wave function for two and three electrons. As the spin of the electron is 1/2, the Young diagrams for the spin part can maximally have two rows, one for each spin direction. The Young diagrams for the spatial part of the wave function are then given as the transpose of the respective spin diagram and, hence, have at most two columns. For two electrons there exist two diagrams corresponding to the singlet (Fig. 1a) and triplet (Fig. 1b) configurations. For three electrons, there exist two diagrams with two electrons in one spin channel
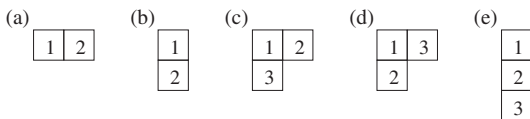

Fig. 1. Possible standard Young diagrams for the spatial part of the wave function for two [figures (a) and (b)] and three [figures (c) to (e)] electrons. There are maximally two columns in each diagram, one for each spin direction. Figures (a) and (b) correspond to the two electron singlet and triplet, respectively. For diagram (c) the wave function is symmetrized for particles 1 and 2 and antisymmetrized for 1 and 3, while for diagram (d) the symmetrization is with respect to particles 1 and 3 and the antisymmetrization with respect to 1 and 2. For diagram (e) the wave function is antisymmetrized with respect to the interchange of any two particles.

and the remaining electron in the other channel (Fig. 1 c and d) and one diagram with all electrons having the same spin (Fig. 1 e).

In practice, we solve the Schrödinger equation in N dimensions and then symmetrize each solution according to the Young diagrams for the given particle number. If none of the Young diagrams yields a non-vanishing solution after symmetrization the state does not describe a solution for spin-1/2 particles and is discarded. If a state yields a non-vanishing contribution for a given diagram the appropriately symmetrized state is normalized and used in further calculations.

The solution of higher dimensional problems within these symmetry restrictions has been implemented in the `octopus` computer program [13,14]. The lowest energy solution is found to be purely symmetric and is, therefore, for $N > 2$, discarded. With increasing number of electrons we also observe an increasing number of states which do not satisfy the fermionic symmetry requirements.

3. Local density approximation

The local density approximation for electrons interacting in one spatial dimension is derived from quantum Monte-Carlo calculations for a 1D homogeneous electron gas where the electrons interact via the soft-Coulomb interaction in Eq. (2)[15]. The correlation energy is parametrized in terms of r_s and the spin polarization $\zeta = (N_\uparrow - N_\downarrow)/N$ in the form

$$\epsilon_c(r_s, \zeta) = \epsilon_c(r_s, \zeta = 0) + \zeta^2 [\epsilon_c(r_s, \zeta = 1) - \epsilon_c(r_s, \zeta = 0)] \tag{4}$$

with

$$\epsilon_c(r_s, \zeta = 0, 1) = -\frac{1}{2} \frac{r_s + E r_s^2}{A + B r_s + C r_s^2 + D r_s^3} \times \ln\left(1 + \alpha r_s + \beta r_s^m\right) \tag{5}$$

which proves to be very accurate in the parameterization for 1D systems for different long-range interactions [16,17,15]. Note, that the above energy is given in Hartree units. To obtain a priori the exact high-density result known from the random-phase approximation, i.e.

$$\epsilon_c(r_s \to 0, \zeta = 0) = -\frac{4}{\pi^4 a^2} r_s^2, \tag{6}$$

$$\epsilon_c(r_s \to 0, \zeta = 1) = -\frac{1}{2\pi^4 a^2} r_s^2, \tag{7}$$

to leading order in r_s, we fix the ratio α/A to be equal to $8/(\pi^4 a^2)$ and $1/(\pi^4 a^2)$ for $\zeta = 0$ and $\zeta = 1$, respectively. In both cases m is limited to values larger than 1. As a result, the number of independent parameters in Eq. (5) is reduced to 7. In addition, for $a = 1$ the denominator can be simplified by setting $B = 0$. However, for smaller values of the softening parameter the linear term in the denominator is important for achieving agreement with the quantum Monte-Carlo results. The optimal values of the parameters are given in Table 1. For more details on the 1D QMC methodology and the parameterization procedure we refer to Refs. [16,17].

We have implemented the 1D LDA for $a = 1$ in both unpolarized and polarized versions in the `octopus` program [13,14].

Fig. 2 shows the linear and non-linear absorption spectra of a 1D Be^{2+} system, i.e. with an external potential of

$$v_{\text{ext}}^{\text{Be}}(x) = \frac{-4}{\sqrt{x^2 + a^2}} \tag{8}$$

containing two electrons. We use the LDA as an adiabatic approximation to the exact time-dependent exchange-correlation potential. The spectrum is calculated in linear response to a spatially constant perturbation at $t = 0$, i.e. we apply an additional external electric field $\mathcal{E}$ in dipole approximation

$$v_{\text{ext}}^{\text{kick}}(x, t) = x \mathcal{E}_0 \delta(t) \tag{9}$$