

# Time-Dependent Two-Particle Reduced Density Matrix Theory: Application to High-Harmonic Generation

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**Abstract.** We simulate the electronic response of atoms to strong laser pulses by propagating the time-dependent two-particle reduced density matrix (TD-2RDM). The propagation of the 2RDM requires carefully designed closure approximations to decouple the equation of motion for the 2RDM from the higher members of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy. Recent improvements in the closure approximation allow the accurate calculation of high-harmonic spectra from beryllium and neon targets where mean field theories such as time-dependent Hartree-Fock and time-dependent density functional theory show sizable discrepancies to multiconfigurational time-dependent Hartree-Fock (MCTDHF) reference calculations. We trace these differences back to the ionization dynamics. We find that the accurate description of the ionization dynamics is the key to achieve agreement with high-harmonic spectra from MCTDHF.

## 1. Introduction

The simulation of multi-electron dynamics in atomic, molecular, or solid state systems is among the most costly calculations in computational physics. The complexity of such simulations originates from the complexity inherent in the many-body wavefunctions. Considerable effort has been dedicated to the development of techniques to calculate ground state properties of large atoms and molecules within the framework of quantum chemistry [1]. One such technique relies on the replacement of the full wavefunction by the 2RDM as the basic working variable [2]. The 2RDM is a considerably “smaller” object that condenses the relevant information stored in the many-body wavefunction into a form that can be handled even for large multi-electronic systems. More specifically, the information content of the 2RDM scales with particle number only polynomially whereas the wavefunction features exponential scaling. This difference in scaling will make the 2RDM a particularly relevant computational tool as computational power continues to increase. Dating back to Bogoliubov [3] the idea to solve the time-dependent many-body problem on the two-particle level has triggered a considerable amount of scientific work [4-11].



It was quickly realized that the exact propagation of the 2RDM depends on the next higher reduced density matrices and any useful application will require the closure of the equations. Such closure schemes, however, were fraught with instabilities ever since. These instabilities occur because giving up on the wavefunction may result in approximate 2RDMs that cannot be associated with an  $N$ -electron wavefunction [10]. This  $N$ -representability problem is, beside the search for accurate closure approximations, a second challenge for the propagation of the 2RDM.

In this work we report on the progress in the development of the time-dependent two-particle reduced density matrix (TD-2RDM) method. We demonstrate its power by simulating the high-harmonic generation (HHG) [12-15] of multi-electronic atomic systems. In particular we investigate the ionization dynamics underlying the HHG process to identify the origin of differences found among various theoretical methods. We perform advanced state-of-the-art multiconfigurational time-dependent Hartree-Fock (MCTDHF) calculations that (if feasible) represent the most accurate approach to the multi-electron dynamics presently available [16]. We find that the TD-2RDM method shows remarkable agreement with MCTDHF reference calculations for the HHG spectrum of neon and beryllium subject to strong laser pulses whereas mean-field methods such as time-dependent Hartree-Fock (TDHF) or time-dependent density functional theory (TDDFT) show clear deviations from the MCTDHF result.

## 2. Theoretical Background

The central proposition of quantum mechanics is that all information on the physical system can be described by the many-body wavefunction  $\Psi(\mathbf{x}_1 \dots \mathbf{x}_N, t)$  where in the case of electrons  $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$  comprises the 3D space coordinate  $\mathbf{r}_i$  and the spin coordinate  $\sigma_i \in \{\uparrow, \downarrow\}$ . However, much of the information stored in the wavefunction is redundant when extracting key properties of the system such as the electronic density, the total energy, the total spin, or pair correlation functions. These quantities can be unambiguously and exactly extracted from the 2RDM,  $D(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}'_1 \mathbf{x}'_2; t)$ , defined by the trace over all but two particles of the bilinear form  $\Psi^* \Psi$  of the  $N$ -electron wavefunction  $\Psi$ ,

$$D_{12} = D(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}'_1 \mathbf{x}'_2; t) = \frac{N!}{(N-2)!} \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3 \dots \mathbf{x}_N, t) \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3 \dots \mathbf{x}_N, t) d\mathbf{x}_3 \dots d\mathbf{x}_N. \quad (1)$$

Following [17], we use for the  $p$ RDM the following short-hand notation

$$D_{1\dots p} = D(\mathbf{x}_1 \dots \mathbf{x}_p; \mathbf{x}'_1 \dots \mathbf{x}'_p; t), \quad (2)$$

where also the time dependence in the notation of the RDMs is dropped for simplicity. With this notation the equation of motion for the 2RDM (the second member of the quantum BBGKY hierarchy) can be written as [3]

$$i\partial_t D_{12} = [H_{12}, D_{12}] + \text{Tr}_3 [W_{13} + W_{23}, D_{123}]. \quad (3)$$

The second term on the right-hand side describes the collision of pairs with the remaining  $N-2$  particles. This scattering process depends on the 3RDM,  $D_{123}$ . Consequently, the 2RDM cannot be propagated without knowledge of the 3RDM. Any application of Eq. (3) requires the closure via a reconstruction [18-20]

$$D_{123} \approx D_{123}^R \{D_{12}\}. \quad (4)$$

We will refer to  $D_{123}^R$  as the reconstruction functional of the 3RDM. Thus, the equation of motion to be solved is

$$i\partial_t D_{12} = [H_{12}, D_{12}] + \text{Tr}_3 [W_{13} + W_{23}, D_{123}^R \{D_{12}\}]. \quad (5)$$

Recently we have shown [10] that contraction consistency

$$\text{Tr}_3 D_{123}^R \{D_{12}\} = (N - 2)D_{12}, \quad (6)$$

of such a reconstruction  $D_{123}^R$  is of central importance for an accurate and consistent closure of the equation of motion for the 2RDM. It assures that constants of motion originating from symmetries of the Hamiltonian are conserved during propagation.

For the reconstruction functional we employ the Nakatsuji-Yasuda (NY) approximation [19] which is based on the diagrammatic expansion of the 3RDM in analogy to many-body Green's functions. The original version [19] is not contraction consistent leading to violation of symmetries when employed in the time-dependent setup. The extension to the contraction consistent NY approximation via the procedure described in [10] and imposing  $N$ -representability constraints are found to be necessary to ensure a stable propagation.

### 3. Results for HHG spectra

As a test of the present TD-2RDM theory we simulate the non-linear many-electron response of Be and Ne subject to ultra-short few-cycle laser pulses of the form

$$F(t) = F_0 \cos(\omega t) \sin^2 \left( \frac{\omega}{2N_c} t \right) \quad 0 \leq t \leq N_c \frac{2\pi}{\omega}, \quad (7)$$

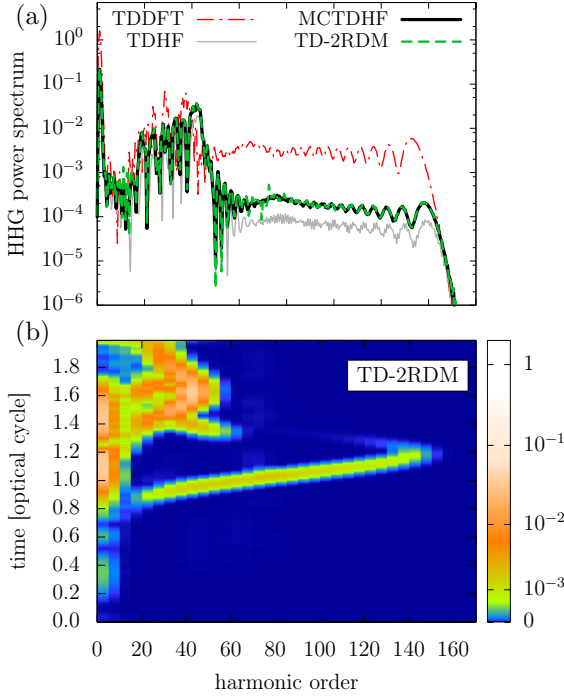
where  $F_0$  is the amplitude of the laser field,  $\omega$  is its mean angular frequency, and  $N_c$  is the number of cycles. In a previous work [10, 11] we observed that the intensity of the HHG spectrum differs significantly among MCTDHF, TDDFT, and TDHF. The TD-2RDM method, on the other hand, predicts HHG radiation that is in remarkable agreement with MCTDHF calculations (see Fig. 1). **The good agreement between the MCTDHF and the TD-2RDM result is remarkable as the TD-2RDM is conceptually an entirely different approach. It shows that the employed reconstruction functional accurately closes the 2RDM equation of motion for this system.** To trace back the significant discrepancies in the HHG yield predicted by the various methods we invoke the semiclassical three-step model [21, 22] and approximate the intensity of the high-harmonic radiation as

$$I^{\text{HHG}}(t_{\text{rec}}) \propto \dot{N}_{\text{ion}}(t_{\text{ion}}) P_{\text{rec}}(t_{\text{rec}}), \quad (8)$$

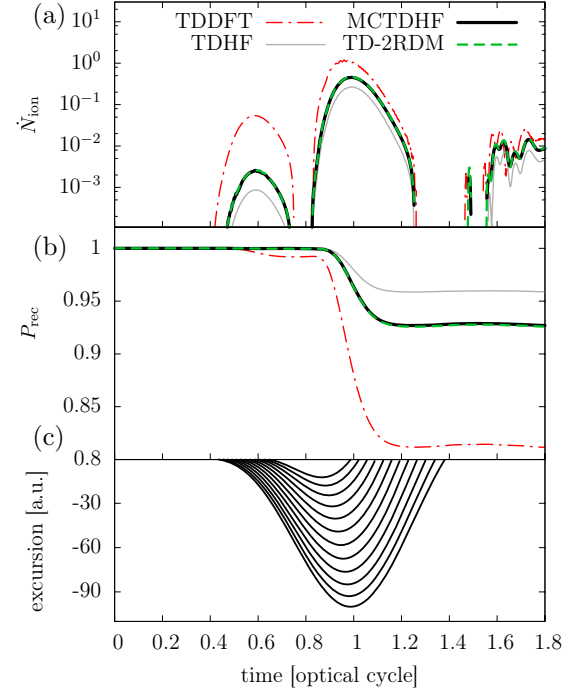
where  $\dot{N}_{\text{ion}}(t_{\text{ion}})$  is the transient ionization rate at ionization time  $t_{\text{ion}}$  and  $P_{\text{rec}}(t_{\text{rec}})$  is the recombination probability at the recombination time  $t_{\text{rec}}$ . In this semiclassical model the electron is ionized from the atom at time  $t_{\text{ion}}$ , then is accelerated in the external laser field, before it recombines with the parent ion at time  $t_{\text{rec}}$ . The ionization rate can be expressed in terms of the electronic density  $\rho(\mathbf{r}, t)$  at time  $t$

$$\dot{N}_{\text{ion}} = \partial_t \int_{|\mathbf{r}| > R} \rho(\mathbf{r}, t) d\mathbf{r}, \quad (9)$$

where in the following the cut-off radius  $R = 20$  a.u.. This value is chosen to be larger than the tunnel ionization radius  $R_t = I_p/F_0 = 5$  a.u. and smaller than the quiver radius  $R_q = F_0/\omega^2 = 54$  a.u. to include all electrons involved in the HHG process. The numerical



**Figure 1.** (a) HHG spectrum for neon subject to a 3-cycle laser pulse with wavelength  $\lambda = 800\text{nm}$  and intensity  $I = 10^{15}\text{W/cm}^2$  (taken from [11]). (b) Time-frequency transformation of the high-harmonic radiation calculated from the TD-2RDM method.



**Figure 2.** (a) The number of electrons ionized per time interval  $\dot{N}_{\text{ion}}(t_{\text{ion}})$  [Eq. (11)] and (b) the recombination probability  $P_{\text{rec}}$  [Eq. (12)] for neon subject to the same laser pulse as shown in Fig. 1. In addition the trajectories that contribute to the high-energy cut-off are shown in (c).

results are, however, insensitive to the precise value of  $R$ . The recombination probability  $P_{\text{rec}}$ , on the other hand, can be approximated as the probability to find no electron to be ionized

$$P_{\text{rec}} = \int_{|\mathbf{r}_1| < R} \dots \int_{|\mathbf{r}_N| < R} |\Psi(\mathbf{x}_1 \dots \mathbf{x}_N, t)|^2 d\mathbf{x}_1 \dots d\mathbf{x}_N. \quad (10)$$

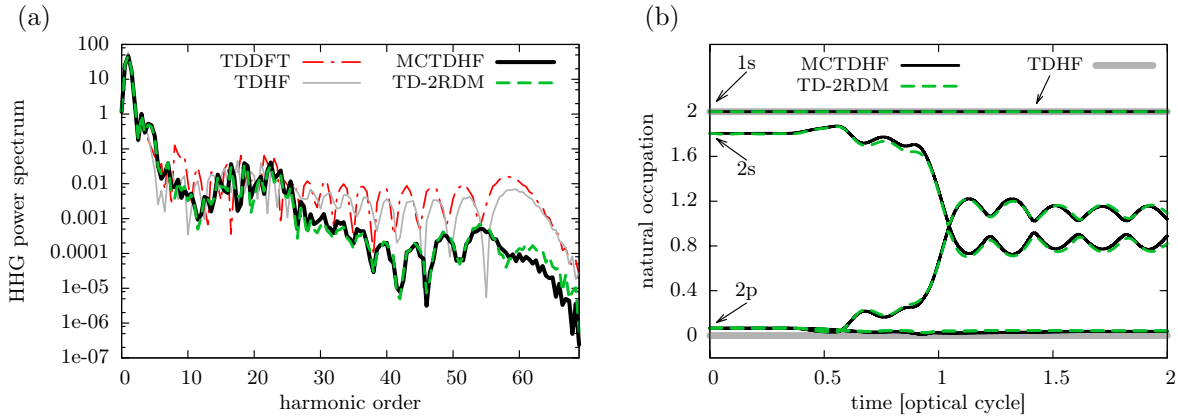
While calculating this quantity in MCTDHF and TDHF is straightforward, it requires more careful consideration within TDDFT and TD-2RDM. In TDDFT we approximate the recombination probability by using the Kohn-Sham wavefunction  $\Psi^{KS}(\mathbf{x}_1 \dots \mathbf{x}_N, t) = |\psi_1^{KS}(\mathbf{x}_1) \dots \psi_N^{KS}(\mathbf{x}_N)|$  in Eq. (10). The validity of this approximation has remained an open question [23, 24]. The TD-2RDM method, on the other hand, has the advantage that if three-particle ionization is negligible it allows to accurately extract this information from the two-particle density as

$$P_{\text{rec}} = 1 - \int_{|\mathbf{r}_1| > R} D(\mathbf{x}_1; \mathbf{x}_1; t) d\mathbf{x}_1 + \int_{|\mathbf{r}_1| > R} \int_{|\mathbf{r}_2| > R} D(\mathbf{x}_1 \mathbf{x}_2; \mathbf{x}_1 \mathbf{x}_2; t) d\mathbf{x}_1 d\mathbf{x}_2, \quad (11)$$

without invoking any read-out functional.

Examining the predictions for  $\dot{N}_{\text{ion}}$  and  $P_{\text{rec}}$  among different methods explains the observed discrepancies in the HHG spectrum. For example, the HHG yield of neon which has a large ionization potential is dominated by the ionization rate  $\dot{N}_{\text{ion}}$ . Focusing on trajectories that

contribute to the high-energy cut-off [see Fig. 2(c)] the ionization rate at early times when these trajectories take off [see Fig. 2(a)] gives a qualitative prediction for the HHG yield at the energy cut-off. For moderate intensities, the recombination probability for neon [Eq. (10)] is close to  $P_{\text{rec}} \approx 1$  among all investigated methods (with the exception of TDDFT) [see Fig. 2(b)] and does not play a decisive role for the HHG yield. The ability of the TD-2RDM method to correctly account for ionization [see Fig. 2(a)] is at the origin of the excellent agreement for the HHG spectrum.



**Figure 3.** (a) HHG spectrum for beryllium subject to a 2-cycle laser pulse with wavelength  $\lambda = 800\text{nm}$  and intensity  $I = 4 \times 10^{14}\text{W/cm}^2$  (taken from [11]). (b) Time-dependent natural occupation numbers during the HHG process depicted in (a). The initial orbital character ( $1s, 2s, 2p$ ) of the natural orbitals is indicated. In TDHF and TDDFT the wavefunction is represented by a single Slater determinant with fixed natural occupation numbers of either 2 or 0.

On a more detailed level, the accurate representation of ionization is related to the ability to represent dynamically varying orbital occupation numbers. This feature becomes particularly important for atoms with smaller ionization potentials such as beryllium. In Fig. 3(a) we show the HHG spectrum of beryllium generated from a 2-cycle pulse with  $I = 4 \times 10^{14}\text{W/cm}^2$ . The time-dependence initiated in the natural occupation numbers is a signature of the strong ionization taking place. Separating one electron from the atom completely while all other electrons remain bound requires the occupation of the initial  $2s$  orbital to drop from two to about one [25] [Fig. 3(b)]. On the level of the TD-2RDM method this time-dependent population transfer is correctly described, whereas in TDDFT and TDHF the occupation numbers remain fixed (in the present case to two). The variation of the natural occupation is one of the essential features that cannot be reproduced by mean-field theories. Although the ionization process may seem, at first glance, to be a rather uncorrelated process it is in fact characterized by the correlated dynamics of the natural occupation numbers. The ability to account for such correlations is key to the success of the TD-2RDM method.

#### 4. Conclusions

We have presented the HHG spectrum of neon and beryllium calculated from the time-dependent two-particle reduced density matrix (TD-2RDM) method and compared with various other methods. As a reference calculation we used the multiconfigurational time-dependent Hartree-Fock method (MCTDHF). We traced the deviations in the HHG spectrum among different methods back to deviations in the ionization probability by employing the semi-classical three-step-model. We found that the high degree of accuracy of the TD-2RDM method and the incorrect predictions by time-dependent density functional theory (TDDFT)

and time-dependent Hartree-Fock (TDHF) are closely related to the ability to correctly describe ionization probabilities. For the accurate description of the ionization process, especially in strong fields, the dynamical population transfer among the natural orbitals plays a decisive role. We have demonstrated that the time dependence of the natural occupation numbers predicted by MCTDHF agrees well with the result from the TD-2RDM method. This feature is a key ingredient for the accurate description of the HHG process.

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