

# Time-dependent renormalized natural orbital theory applied to the two-electron spin-singlet case: Ground state, linear response, and autoionization

M. Brics and D. Bauer\*

*Institut für Physik, Universität Rostock, 18051 Rostock, Germany*

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Favorably scaling numerical time-dependent many-electron techniques such as time-dependent density functional theory (TDDFT) with adiabatic exchange-correlation potentials typically fail in capturing highly correlated electron dynamics. We propose a method based on natural orbitals, i.e., the eigenfunctions of the one-body reduced density matrix, that is almost as inexpensive numerically as adiabatic TDDFT, but which is capable of describing correlated phenomena such as doubly excited states, autoionization, Fano profiles in the photoelectron spectra, and strong-field ionization in general. Equations of motion (EOMs) for natural orbitals and their occupation numbers have been derived earlier. We show that by using renormalized natural orbitals (RNOs) both can be combined into one equation governed by a hermitian effective Hamiltonian. We specialize on the two-electron spin-singlet system, known as being a “worst case” testing ground for TDDFT, and employ the widely used, numerically exactly solvable, one-dimensional helium model atom (in a laser field) to benchmark our approach. The solution of the full, nonlinear EOMs for the RNOs is plagued by instabilities, and resorting to linear response is not an option for the ultimate goal to study nonperturbative dynamics in intense laser fields. We therefore make two rather bold approximations: we employ the initial-state-“frozen” effective RNO Hamiltonian for the time propagation and truncate the number of RNOs to only two per spin. Surprisingly, it turns out that even with these strong approximations we obtain a highly accurate ground state, reproduce doubly excited states, and autoionization.

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## I. INTRODUCTION

The “holy grail” of computational many-body theory is to overcome the so-called “exponential wall,” i.e., the exponentially increasing numerical effort as a function of the particle number to solve the many-body Schrödinger equation [1]. It is an obvious idea that one should try to replace the high-dimensional many-body wave function by some simpler, lower-dimensional quantity, and then derive equations governing this quantity because the “many-electron wave function tells us more than we need to know” [2]. Reduced density matrices (RDMs) appear to be most suitable for that purpose. In fact, extensive research has been devoted to the properties and applications of RDMs, starting with the classic work by Löwdin [3], already early summarized in [4], and meanwhile covered in books and reviews [5–9], and excellent thesis works [10,11].

For systems with two-body interactions, any observable can be *explicitly* written down in terms of the two-body reduced density matrix (2RDM). The Hohenberg-Kohn theorem [12] of density functional theory (DFT) (see, e.g., [13]) even ensures that any observable (of a system governed by a Hamiltonian with a scalar, local, external potential) is *in principle* a functional of the single-particle density, i.e., the diagonal of the (spin-integrated) one-body reduced density matrix (1RDM). However, these functionals are not known for all observables of interest so that approximations have to be made in practice. Quite reasonably, it seems that the more reduced the quantity employed is, the more approximations have to be made in the governing equations (such as the intricate exchange-

correlation (xc) potential in the Kohn-Sham scheme [14]), and for the observables. Employing the 1RDM as the basic “variable” instead of the single-particle density brings us to reduced density-matrix functional theory (RDMFT) [3–8,10,11]. In RDMFT, the Bogoliubov-Born-Green-Kirkwood-Yvon chain of equations needs to be truncated by a (sufficiently accurate) approximation of the 2RDM as a functional of the 1RDM. In the simplest form, this leads just to the Hartree-Fock (HF) equations. Expressions for the 2RDM beyond HF have been devised and applied (see, e.g., [15–19]), although relatively few compared to the abundant literature on xc potentials in DFT. Approaches using directly the 2RDM as the basic variable have been proposed and applied as well [9]. A naive minimization of the energy as a functional of the 2RDM will, however, yield too low energy values, as not all two-matrices (2Ms) originate from an  $N$ -electron state. Recent progress in the solution of this so-called  $N$ -representability problem has been made by formulating a hierarchy of conditions a 2M has to fulfill in order to be a proper 2RDM (without resorting to higher-order RDMs) [20].

It is computationally beneficial to expand the 1RDM and 2RDM in 1RDM eigenfunctions, the so-called natural orbitals (NOs) [3], as they form the best possible basis set (in a well-defined mathematical sense; see, e.g., [5,11] for details). The resulting equations for these NOs form a set of coupled, nonlinear Schrödinger-like equations [21], as in configuration interaction calculations. The eigenvalue of the 1RDM to which a NO belongs can be interpreted as its occupation number (OCN). Unlike in, e.g., Hartree-Fock, these OCNs are, in general, fractional  $\in ]0,1[$  in correlated fermionic systems (unless they are “pinned” to 0 or 1 [22,23]).

In this work, we investigate whether NOs can be efficiently employed to describe the correlated *dynamics* of a two-electron

\*Corresponding author: [dieter.bauer@uni-rostock.de](mailto:dieter.bauer@uni-rostock.de)

spin-singlet system in an external, driving field such as that of a laser. Of course, the study of the *structure* of correlated two-electron systems has a long history that started soon after the “invention” of quantum mechanics. In view of a NO description it has been analyzed by Löwdin and Shull in 1956 [24]. The two-electron spin-singlet ground-state wave function has an exceptionally simple structure when expanded in NOs, as the coefficient matrix turns out to be diagonal. This means that the ground-state two-body density matrix (2DM) needs not be approximated in terms of the NOs but is known exactly in the two-electron case.

One may think that the two-electron case is a bit (too) trivial to test a novel time-dependent *many*-body method. However, this is not the case. While electronic structure calculations are difficult enough, time-dependent quantum dynamics beyond linear response with nonperturbative drivers is by far more challenging. In fact, from a computational point of view it is orders of magnitude more demanding because on top of the ground-state problem one, subsequently, needs to propagate the system for typically  $10^3$ – $10^4$  time steps on numerical grids typically  $10^2$ – $10^3$  times larger than that for the ground state. It is thus even more important to develop efficient numerical methods capable of describing such strongly driven quantum dynamics. Time-dependent density functional theory (TDDFT) [25,26] works well in many cases but fails (with known and practicable adiabatic xc potentials) whenever the processes to be described rely on strong correlation or involve resonant interaction [27–35]. As the correlation energy (relative to the total energy) typically increases as the number of electrons decreases (down to 2), it is the *few*-body correlated electron dynamics that serve as “worst case” benchmarks for methods beyond TDDFT with adiabatic xc potentials. For instance, autoionization in strong laser fields is currently investigated experimentally [36,37] and particularly challenging for theory because it involves multiply excited states. As multiply excited states are absent in TDDFT using adiabatic xc potentials [25,38] it serves as an ideal testing ground for novel *ab initio* methods going beyond “standard” TDDFT.

An algorithm for propagating NOs and OCNs for two coupled nonlinear oscillators has been proposed in [39]. The general equations of motion (EOM) for the NOs and their OCNs have been derived in [40] (see also [10]). However, the volume of published work on *time-dependent* density matrix functional theory (TDDMFT) is still very limited. Different adiabatic approximations to TDDMFT have been derived and applied to molecules [41–44] and a two-site Hubbard model [45], respectively. Exact time-dependent NO occupations have been investigated [46] using the same numerically exactly solvable model atom employed in the current work. It was found that common approximations for the 2RDM functional render the OCN constant, which is incorrect for, e.g., atoms in strong laser pulses or resonant interactions [33]. A semiclassical approach to propagate the 1RDM that allows for changing OCNs has been proposed in [47] and applied to Moshinsky’s two-electron model atom [48].

Our paper is organized as follows. In Sec. II we review the basic density matrix and NO theory for the two-electron case and introduce renormalized NOs (RNOs), which allow us to unify the EOMs for the OCNs and the NOs. Further,

we specialize in the spin-singlet case, briefly discuss the time-dependent Hartree-Fock limit, and derive variationally the equations governing the RNO ground-state configuration. In Sec. III we present results for two RNOs per spin. After the ground state is obtained, the linear-response spectrum and autoionization in a laser field are investigated. We conclude and give an outlook in Sec. IV. Details of the derivation of the EOMs for the NOs are given in Appendix A, the relation between the expansion coefficients of the ground-state 2DM and those of the two-electron spin singlet ground state is given in Appendix B. Atomic units are used throughout.

## II. THEORY

The hermitian 2DM for a two-electron system with wave function  $\Phi(12; t)$  reads

$$\gamma_2(12, 1'2'; t) = \Phi^*(1'2'; t)\Phi(12; t), \quad (1)$$

where the arguments 1, 2, 1', etc., comprise spatial and spin degrees of freedom  $(x_1, \sigma_1)$ ,  $(x_2, \sigma_2)$ ,  $(x'_1, \sigma'_1)$  ... The hermitian 1RDM is

$$\gamma_1(1, 1'; t) = 2 \int d2 \gamma_2(12, 1'2; t). \quad (2)$$

Given a Hamiltonian for the two-electron time-dependent Schrödinger equation (TDSE),

$$i \partial_t \Phi(12; t) = \hat{H}(12; t)\Phi(12; t), \quad (3)$$

of the form

$$\hat{H}(12; t) = \hat{h}_0(1; t) + \hat{h}_0(2; t) + v_{ee}(12), \quad (4)$$

where  $v_{ee}$  is the electron-electron interaction, the 2DM fulfills the von Neumann equation, while the 1RDM obeys the EOM

$$\begin{aligned} -i \partial_t \gamma_1(1, 1'; t) &= [\hat{h}_0(1') - \hat{h}_0(1)]\gamma_1(1, 1'; t) \\ &+ 2 \int d2 \{v_{ee}(1'2) - v_{ee}(12)\}\gamma_2(12, 1'2; t). \end{aligned} \quad (5)$$

The hermitian 1RDM can be written in terms of an orthonormalized set of NOs,  $\phi_k$ ,  $k = 1, 2, 3, \dots$ , and real, positive-definite OCNs  $n_k$  as

$$\gamma_1(1, 1'; t) = \sum_k n_k(t) \phi_k^*(1'; t) \phi_k(1; t), \quad (6)$$

$$\sum_k n_k(t) = 2, \quad \int d1 |\phi_k(1; t)|^2 = 1. \quad (7)$$

In other words,  $\phi_k$  is the eigenvector of  $\gamma_1$  with respect to the eigenvalue  $n_k$ ,

$$\int d1' \gamma_1(1, 1'; t) \phi_k(1'; t) = n_k(t) \phi_k(1; t). \quad (8)$$

As the NOs form a complete basis one can expand the 2DM in them,

$$\gamma_2(12, 1'2'; t) = \sum_{ijkl} \gamma_{2,ijkl}(t) \phi_i(1; t) \phi_j(2; t) \phi_k^*(1'; t) \phi_l^*(2'; t). \quad (9)$$

### A. Equation of motion for renormalized natural orbitals

We find it numerically beneficial to incorporate the OCNs into the NOs by renormalizing them,

$$\tilde{\phi}_k(1;t) = \sqrt{n_k(t)} \phi_k(1;t), \quad (10)$$

$$\int d1 |\tilde{\phi}_k(1;t)|^2 = n_k(t). \quad (11)$$

Inserting the NO expansions of the density matrices  $\gamma_1$  and  $\gamma_2$ , (6) and (9), respectively, into the EOM for the 1RDM (5),

$$\begin{aligned} i \partial_t \tilde{\phi}_n(1;t) = & -\frac{1}{n_n(t)} \left\{ 2 \operatorname{Re} \sum_{jkl} \tilde{\gamma}_{2,njkl}(t) \langle \tilde{k}(t) \tilde{l}(t) | v_{ee} | \tilde{n}(t) \tilde{j}(t) \rangle + \langle \tilde{n}(t) | \hat{h}_0(t) | \tilde{n}(t) \rangle \right\} \tilde{\phi}_n(1;t) \\ & + \sum_{k \neq n} \frac{2}{n_k(t) - n_n(t)} \sum_{jpl} \{ \tilde{\gamma}_{2,kjpl}(t) \langle \tilde{p}(t) \tilde{l}(t) | v_{ee} | \tilde{n}(t) \tilde{j}(t) \rangle - [\tilde{\gamma}_{2,njpl}(t) \langle \tilde{p}(t) \tilde{l}(t) | v_{ee} | \tilde{k}(t) \tilde{j}(t) \rangle]^* \} \tilde{\phi}_k(1;t) \\ & + \hat{h}_0(1;t) \tilde{\phi}_n(1;t) + 2 \sum_k \sum_{jl} \tilde{\gamma}_{2,kjnl}(t) \langle \tilde{l}(t) | v_{ee} | \tilde{j}(t) \rangle (1;t) \tilde{\phi}_k(1;t). \end{aligned} \quad (13)$$

Here, we used the abbreviations

$$\tilde{\gamma}_{2,njkl}(t) = \frac{\gamma_{2,njkl}(t)}{\sqrt{n_n(t)n_j(t)n_k(t)n_l(t)}}, \quad (14)$$

$$\langle \tilde{l}(t) | v_{ee} | \tilde{j}(t) \rangle (1;t) = \int d1' \tilde{\phi}_l^*(1';t) v_{ee}(11') \tilde{\phi}_j(1';t), \quad (15)$$

$$\begin{aligned} & \langle \tilde{k}(t) \tilde{l}(t) | v_{ee} | \tilde{n}(t) \tilde{j}(t) \rangle \\ & = \int d1 \tilde{\phi}_k^*(1;t) \langle \tilde{l}(t) | v_{ee} | \tilde{j}(t) \rangle (1;t) \tilde{\phi}_n(1;t). \end{aligned} \quad (16)$$

With (11), Eq. (13) is a set of coupled EOMs for the RNOs alone.

Multiplication of (13) by  $\tilde{\phi}_n^*(1;t)$  and integration  $\int d1$  yields

$$\dot{n}_n(t) = -4 \operatorname{Im} \sum_{jkl} \tilde{\gamma}_{2,njkl}(t) \langle \tilde{k}(t) \tilde{l}(t) | v_{ee} | \tilde{n}(t) \tilde{j}(t) \rangle, \quad (17)$$

which, expressed in terms of NOs instead of RNOs, has been derived earlier [40]. This equation is useful to see whether a certain approximation of  $\tilde{\gamma}_{2,njkl}$  will lead to time-varying OCNs or constant OCNs. For instance, common approximations of the form

$$\tilde{\gamma}_{2,njkl}^{(\text{approx})}(t) = f_{njkl}(t) \delta_{nk} \delta_{jl} - g_{njkl}(t) \delta_{nl} \delta_{jk} \quad (18)$$

with  $f_{njkl}(t)$  and  $g_{njkl}(t)$  real will lead to constant OCNs,  $\dot{n}_n(t) \equiv 0$ , because all NO phases that could lead to an imaginary part on the right-hand side of (17) cancel. From the exact numerical solution of the two-electron TDSE we know that for, e.g., resonant interactions (Rabi floppings) and in other scenarios, the OCNs *do* change in time [33,46,47].

If the total number of particles is conserved,

$$0 = \operatorname{Im} \sum_{njkl} \tilde{\gamma}_{2,njkl}(t) \langle \tilde{k}(t) \tilde{l}(t) | v_{ee} | \tilde{n}(t) \tilde{j}(t) \rangle \quad (19)$$

coupled EOMs for the NOs and OCNs have been derived and reviewed in the literature [10,11,40].

We have derived a single EOM that is particularly useful for our purposes. It has the form

$$i \partial_t \tilde{\Phi}(1;t) = \hat{\mathcal{H}}(1;t) \tilde{\Phi}(1;t) \quad (12)$$

with a hermitian Hamiltonian  $\hat{\mathcal{H}}$  and a column vector  $\tilde{\Phi}(1;t)$  with the RNO  $\tilde{\phi}_k(1;t)$  in it. The derivation is given in Appendix A, the result being

follows from (17) upon summing over  $n$ . Moreover, one finds that the RNOs stay mutually orthogonal if

$$\mathcal{D}_{nm}(t) = \mathcal{D}_{mn}^*(t) \quad (20)$$

holds, where

$$\mathcal{D}_{nm}(t) = \sum_{kjl} \tilde{\gamma}_{2,kjnl}(t) \langle \tilde{m}(t) \tilde{l}(t) | v_{ee} | \tilde{k}(t) \tilde{j}(t) \rangle. \quad (21)$$

As the RNOs, being  $\forall t$  eigenfunctions of a hermitian matrix, *should* stay orthogonal, Eq. (20) poses a condition any approximation of  $\tilde{\gamma}_{2,kjnl}(t)$  has to fulfill.

### B. Two-electron spin-singlet case

If the two-electron wave function is  $\forall t$  of the spin-singlet form

$$\Phi(12;t) = \Phi(x_1 x_2;t) \frac{1}{\sqrt{2}} (\delta_{\sigma_1+} \delta_{\sigma_2-} - \delta_{\sigma_1-} \delta_{\sigma_2+}), \quad (22)$$

$\Phi(x_1 x_2;t) = \Phi(x_2 x_1;t)$  (with “+” and “-” for “spin up” and “spin down,” respectively), we have with (1) and

$$\gamma_1(x_1, x'_1;t) = 2 \int dx_2 \Phi^*(x'_1 x_2;t) \Phi(x_1 x_2;t) \quad (23)$$

that

$$\gamma_1(1, 1';t) = \frac{1}{2} \gamma_1(x_1, x'_1;t) (\delta_{\sigma_1+} \delta_{\sigma'_1+} + \delta_{\sigma_1-} \delta_{\sigma'_1-}). \quad (24)$$

We switch temporarily back to NOs normalized to unity. Making the ansatz

$$\phi_k(x\sigma;t) = \phi_k(x;t) (a_k \delta_{\sigma+} + b_k \delta_{\sigma-}), \quad (25)$$

$$|a_k|^2 + |b_k|^2 = 1, \quad \int dx |\phi_k(x;t)|^2 = 1, \quad (26)$$

one simply finds the same form for the spin-reduced IRDM as in (6),

$$\gamma_1(x, x'; t) = \sum_k n_k(t) \phi_k^*(x'; t) \phi_k(x; t). \quad (27)$$

Because of orthonormality of the NOs, for  $k \neq k'$

$$(a_{k'}^* a_k + b_{k'}^* b_k) \int dx \phi_{k'}^*(x; t) \phi_k(x; t) = 0 \quad (28)$$

need to be fulfilled so that either the spatial part of the NOs must be orthogonal or the spin part. For a given spin part of  $\phi_k$  with coefficients  $a_k$  and  $b_k$  one can always find (up to an irrelevant phase factor) a normalized spin part ( $a_{k'} \delta_{\sigma_+} + b_{k'} \delta_{\sigma_-}$ ) of  $\phi_{k'}$  that is orthogonal to ( $a_k \delta_{\sigma_+} + b_k \delta_{\sigma_-}$ ). A convenient choice is  $a_k = 1, b_k = 0, a_{k'} = 0, b_{k'} = 1$  while  $\phi_{k'}(x; t) = \phi_k(x; t)$ . In other words, the spatial NOs appear pairwise equal, with opposite spin parts. This is probably the most trivial example of a *pairing* phenomenon. One may order the NOs such that for odd  $k$  the following equations hold:

$$\phi_k(x\sigma; t) = \phi_k(x; t) \delta_{\sigma_+}, \quad k = 1, 3, 5, \dots, \quad (29)$$

$$\phi_k(x; t) = \phi_{k+1}(x; t), \quad (30)$$

$$\phi_{k+1}(x\sigma; t) = \phi_{k+1}(x; t) \delta_{\sigma_-} = \phi_k(x; t) \delta_{\sigma_-}. \quad (31)$$

Then we can write instead of (27)

$$\gamma_1(x, x'; t) = 2 \sum_{k \text{ odd}} n_k(t) \phi_k^*(x'; t) \phi_k(x; t), \quad (32)$$

and we need to consider only half of the NOs (i.e., those with, e.g., the odd indices, i.e., spin up) in the following.

Because the spatial spin-singlet wave function is symmetric it can be shown [11] that its expansion in NOs is diagonal,

$$\Phi(x_1 x_2; t) = \sum_{i \text{ odd}} D_i(t) \phi_i(x_1; t) \phi_i(x_2; t), \quad (33)$$

where, because of (23) and (27),

$$|D_i(t)|^2 = n_i(t). \quad (34)$$

We can thus use the NO expansion coefficients for the wave function  $D_i(t)$  instead of resorting to the NO expansion coefficients  $\gamma_{2, n_j k l}(t)$  for the 2DM. How both are connected is discussed in Appendix B. Formally, in Eq. (33) the time-dependent spatial two-electron wave function is written as a single *geminal* [49], expanded in time-dependent NOs.

The EOMs for the spatial RNOs in terms of the time-dependent geminal expansion coefficients  $D_i$  can be written as (from now on all time arguments are suppressed for brevity)

$$i \partial_t \tilde{\phi}_n(x) = \hat{\mathcal{H}}_n^0(x) \tilde{\phi}_n(x) + \sum_{k \text{ odd} \neq n} \mathcal{H}_{nk}^1(x) \tilde{\phi}_k(x), \quad (35)$$

where

$$\hat{\mathcal{H}}_n^0(x) = A_n + \hat{\mathcal{K}}_n^0(x), \quad (36)$$

$$\mathcal{H}_{nk}^1(x) = B_{nk} + \mathcal{K}_{nk}^1(x) \quad (37)$$

with

$$\begin{aligned} A_n &= -\frac{1}{n_n} \left[ \text{Re} \left( \sum_{k \text{ odd}} \frac{D_n D_k^*}{n_n n_k} \langle \tilde{k} \tilde{k} | v_{ee} | \tilde{n} \tilde{n} \rangle_x \right) + \langle \tilde{n} | \hat{h}_0 | \tilde{n} \rangle_x \right], \\ \hat{\mathcal{K}}_n^0(x) &= \hat{h}_0(x) + \frac{\langle \tilde{n} | v_{ee} | \tilde{n} \rangle_x(x)}{n_n}, \\ B_{nk} &= \frac{1}{n_k - n_n} \sum_{p \text{ odd}} \left( \frac{D_k D_p^*}{n_k n_p} \langle \tilde{p} \tilde{p} | v_{ee} | \tilde{n} \tilde{k} \rangle_x \right. \\ &\quad \left. - \left[ \frac{D_n D_p^*}{n_n n_p} \langle \tilde{p} \tilde{p} | v_{ee} | \tilde{k} \tilde{n} \rangle_x \right]^* \right), \\ \mathcal{K}_{nk}^1(x) &= \frac{D_k D_n^*}{n_k n_n} \langle \tilde{n} | v_{ee} | \tilde{k} \rangle_x(x), \end{aligned} \quad (38)$$

and the potentials  $\langle \tilde{n} | v_{ee} | \tilde{k} \rangle_x(x)$  and matrix elements  $\langle \tilde{p} \tilde{p} | v_{ee} | \tilde{n} \tilde{k} \rangle_x$  defined as in (15) and (16) but all integrals with respect to position space only. Here we exploit that the electron-electron interaction does not directly involve the spin degrees of freedom.

### C. Time-dependent Hartree-Fock limit

Equations (35)–(39) reduce to the two-electron spin-singlet Hartree-Fock limit for  $n_1 = n_2 = 1$ ,  $\tilde{\phi}_1(x) = \phi_1(x) = \tilde{\phi}_2(x) = \phi_2(x)$ , and all other OCNs (and thus RNOs) zero. The (in the NO index) off-diagonal part of the Hamiltonian  $\mathcal{H}_{nk}^1(x)$  in (35) therefore vanishes, and

$$A_1 = -(11|v_{ee}|11)_x - \langle 1 | \hat{h}_0 | 1 \rangle_x,$$

$$\hat{\mathcal{K}}_1^0(x) = \hat{h}_0(x) + \langle 1 | v_{ee} | 1 \rangle_x(x)$$

so that

$$i \partial_t \phi_1(x) = [\hat{h}_0(x) + \langle 1 | v_{ee} | 1 \rangle_x(x) + A_1] \phi_1(x),$$

which is indeed the time-dependent Hartree-Fock (TDHF) equation for the two-electron spin-singlet system (where the Fock term cancels half of the Hartree). In the case of the two-electron spin-singlet system TDHF is equivalent to a time-dependent Kohn-Sham (TDKS) treatment in “exact-exchange approximation” (EXA) and the correlation potential set to zero. Note that, unlike in the general case with more than one NO per spin, the purely time-dependent term  $A_1$  can be eliminated via a contact transformation  $\phi_1(x) \rightarrow \phi_1(x) \exp[-i \int^t A_1(t') dt']$  here.

### D. Ground state

A time-dependent calculation most often starts from the ground state. As we need anyway a code that propagates the RNOs in time according (35) it would be convenient to use imaginary-time propagation for finding the ground state, as is commonly done in TDSE solvers. On the other hand, it must be possible to derive the ground state in terms of RNOs via a minimization approach. We show now that both ways will indeed lead to the same result.

The ground-state energy to be minimized is

$$E = \int d1 [\hat{h}_0(1')\gamma_1(1',1)]_{1'=1} + \int d1 \int d2 v_{ee}(|1-2|)\gamma_2(12,12). \quad (40)$$

Expressed in RNOs, the energy becomes

$$E = 2 \sum_{i \text{ odd}} \langle \tilde{i} | \hat{h}_0 | \tilde{i} \rangle_x + \sum_{i \text{ odd}} \sum_{j \text{ odd}} \frac{e^{i(\varphi_j - \varphi_i)}}{\sqrt{\langle \tilde{i} | \tilde{i} \rangle_x \langle \tilde{j} | \tilde{j} \rangle_x}} \langle \tilde{i} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle_x, \quad (41)$$

where we introduced the phases  $\varphi_i$  via [cf. Eq. (34)]

$$D_i = \sqrt{n_i} e^{i\varphi_i} \quad (42)$$

and explicitly write

$$n_i = \langle \tilde{i} | \tilde{i} \rangle_x. \quad (43)$$

We define a functional  $\tilde{E}[\{\tilde{i}\}, \{\tilde{i}\}]$  that takes the constraint  $\sum_{i \text{ odd}} \langle \tilde{i} | \tilde{i} \rangle = \sum_{i \text{ odd}} n_i = 1$  via the Lagrange parameter  $\epsilon$  into account, the orthogonality of the RNOs via  $\lambda_{ij}$ ,  $\lambda_{ii} = 0$ , the condition  $n_i \geq 0$  via  $\epsilon_i^0$ , and  $n_i \leq 1$  through  $\epsilon_i^1$  (Karush-Kuhn-Tucker conditions, see, e.g., [11,50]),

$$\begin{aligned} \tilde{E} = & 2 \sum_{i \text{ odd}} \langle \tilde{i} | \hat{h}_0 | \tilde{i} \rangle + \sum_{i \text{ odd}} \sum_{j \text{ odd}} \frac{e^{i(\varphi_j - \varphi_i)}}{\sqrt{\langle \tilde{i} | \tilde{i} \rangle \langle \tilde{j} | \tilde{j} \rangle}} \langle \tilde{i} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle \\ & - \epsilon \left( \sum_{i \text{ odd}} \langle \tilde{i} | \tilde{i} \rangle - 1 \right) - \sum_{i \text{ odd}} \sum_{j \text{ odd} \neq i} \lambda_{ij} \langle \tilde{i} | \tilde{j} \rangle \\ & - \sum_{i \text{ odd}} [\epsilon_i^0 \langle \tilde{i} | \tilde{i} \rangle + \epsilon_i^1 (1 - \langle \tilde{i} | \tilde{i} \rangle)]. \end{aligned} \quad (44)$$

Here, we dropped the index  $x$  at  $\langle \cdot | \cdot \rangle_x$ . The ‘‘slackness conditions’’ are [11]

$$\epsilon_i^0 n_i = \epsilon_i^0 \langle \tilde{i} | \tilde{i} \rangle = 0, \quad \epsilon_i^1 (1 - n_i) = \epsilon_i^1 (1 - \langle \tilde{i} | \tilde{i} \rangle) = 0. \quad (45)$$

Actually, the energy functional  $\tilde{E}$  depends not only on the RNOs but also on the phases  $\{\varphi_j\}$  of the geminal expansion coefficients. We suppress this dependence here because the values of these phases for the He spin-singlet ground-state case are already known [see Eq. (73) below]. A more general approach to the ground-state problem based on geminals (where these phases are part of the minimization procedure) has been proposed and applied in [49,51].

A variation of  $\tilde{E}$  with respect to  $\langle \tilde{k} |$  and  $|\tilde{k}\rangle$  leads with

$$\epsilon_k = \epsilon + \epsilon_k^0 - \epsilon_k^1 \quad (46)$$

to

$$\begin{aligned} \epsilon_k |\tilde{k}\rangle = & \left\{ 2 \left[ \hat{h}_0 + \frac{1}{n_k} \langle \tilde{k} | v_{ee} | \tilde{k} \rangle (x) \right] \right. \\ & \left. - \frac{1}{n_k} \text{Re} \left[ \sum_{j \text{ odd}} \frac{D_j D_k^* \langle \tilde{k} \tilde{k} | v_{ee} | \tilde{j} \tilde{j} \rangle}{n_k n_j} \right] \right\} |\tilde{k}\rangle \\ & + \sum_{j \text{ odd} \neq k} \left\{ 2 \frac{D_j D_k^*}{n_j n_k} \langle \tilde{k} | v_{ee} | \tilde{j} \rangle (x) - \lambda_{kj} \right\} |\tilde{j}\rangle, \end{aligned} \quad (47)$$

and the hermitian conjugate of it. Multiplying by  $\langle \tilde{i} |$  from the left (and the hermitian conjugate by  $|\tilde{i}\rangle$  from the right) leads for  $i = k$  to

$$\begin{aligned} \epsilon_i = & \frac{1}{n_i} \left( 2 \langle \tilde{i} | \hat{h}_0 | \tilde{i} \rangle + \sum_{j \text{ odd}} \left\{ 2 \frac{D_j D_i^*}{n_i n_j} \langle \tilde{i} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle \right. \right. \\ & \left. \left. - \text{Re} \left[ \frac{D_j D_i^*}{n_i n_j} \langle \tilde{i} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle \right] \right\} \right), \end{aligned} \quad (48)$$

$$\forall i \quad 0 = \text{Im} \sum_{j \text{ odd}} \frac{D_j D_i^*}{n_j} \langle \tilde{i} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle, \quad (49)$$

and for  $i \neq k$  to

$$\lambda_{ki} = \frac{2}{n_i} \left[ \langle \tilde{i} | \hat{h}_0 | \tilde{k} \rangle + \sum_{j \text{ odd}} \frac{D_j D_k^*}{n_k n_j} \langle \tilde{k} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle \right] = \lambda_{ik}^*, \quad (50)$$

$$\lambda_{ik} = \frac{2}{n_k} \left[ \langle \tilde{k} | \hat{h}_0 | \tilde{i} \rangle + \sum_{j \text{ odd}} \frac{D_j D_i^*}{n_i n_j} \langle \tilde{i} \tilde{k} | v_{ee} | \tilde{j} \tilde{j} \rangle \right]. \quad (51)$$

From this follows

$$\begin{aligned} \langle \tilde{k} | \hat{h}_0 | \tilde{i} \rangle = & \frac{1}{n_i - n_k} \sum_{j \text{ odd}} \frac{1}{n_j} \\ & \times (D_k D_j^* \langle \tilde{j} \tilde{j} | v_{ee} | \tilde{k} \tilde{i} \rangle - D_j D_i^* \langle \tilde{i} \tilde{k} | v_{ee} | \tilde{j} \tilde{j} \rangle), \end{aligned} \quad (52)$$

which can be used to remove  $\hat{h}_0$  entirely from the off-diagonal (with respect to the NO index) part of the Hamiltonian.

Putting Eqs. (47)–(52) together we can write

$$0 = \hat{\mathcal{H}}_n^{00}(x) \tilde{\phi}_n(x) + \sum_{k \text{ odd} \neq n} \mathcal{H}_{nk}^{01}(x) \tilde{\phi}_k(x),$$

$$\hat{\mathcal{H}}_n^{00}(x) = A_n^0 + \hat{\mathcal{K}}_n^{00}(x), \quad (53)$$

$$\mathcal{H}_{nk}^{01}(x) = B_{nk}^0 + \mathcal{K}_{nk}^{01}(x)$$

with

$$A_n^0 = -\frac{1}{n_n} \left( \langle \tilde{n} | \hat{h}_0 | \tilde{n} \rangle + \text{Re} \sum_{k \text{ odd}} \frac{D_k D_n^*}{n_n n_k} \langle \tilde{n} \tilde{n} | v_{ee} | \tilde{k} \tilde{k} \rangle \right),$$

$$\hat{\mathcal{K}}_n^{00}(x) = \hat{h}_0 + \frac{1}{n_n} \langle \tilde{n} | v_{ee} | \tilde{n} \rangle (x), \quad (54)$$

$$\begin{aligned} B_{nk} = & \frac{1}{n_k - n_n} \sum_{p \text{ odd}} \left( \frac{D_k D_p^*}{n_k n_p} \langle \tilde{p} \tilde{p} | v_{ee} | \tilde{k} \tilde{n} \rangle \right. \\ & \left. - \frac{D_p D_n^*}{n_n n_p} \langle \tilde{n} \tilde{k} | v_{ee} | \tilde{p} \tilde{p} \rangle \right), \end{aligned}$$

$$\mathcal{K}_{nk}^{01}(x) = \frac{D_k D_n^*}{n_k n_n} \langle \tilde{n} | v_{ee} | \tilde{k} \rangle (x). \quad (55)$$

Hence, we obtain by this variational method indeed the time-independent, ground-state analog of Eqs. (35)–(39). This allows for finding the RNO ground-state configuration (for a given set of OCNs) by imaginary time propagation of the time-dependent Schrödinger-like, nonlinear equation (35) (see Sec. III A below).

The  $\epsilon_k$  in (47) play the role of orbital energies. Unless the OCNs are pinned to  $n_k = 0$  or 1 we have noninteger  $0 < n_k < 1$  for correlated systems. In such cases Eqs. (45) imply  $\epsilon_k^0 = 0$ ,

$\epsilon_k^1 = 0$  so that

$$\epsilon_k = \epsilon, \quad (56)$$

i.e., all orbital energies are equal. The ground-state RNOs and wave-function expansion coefficients  $D_j$  can be chosen real. Thus we have with (48)

$$\forall i \quad \epsilon = \epsilon_i = \frac{1}{n_i} \left( 2 \langle \tilde{i} | \hat{h}_0 | \tilde{i} \rangle + \sum_{j \text{ odd}} \frac{D_j D_i}{n_i n_j} \langle \tilde{i} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle \right) \quad (57)$$

and thus

$$\sum_{i \text{ odd}} \epsilon_i n_i = \epsilon \sum_{i \text{ odd}} n_i = \epsilon = E \quad (58)$$

because the total energy is, according to (41),

$$E = 2 \sum_{i \text{ odd}} \langle \tilde{i} | \hat{h}_0 | \tilde{i} \rangle + \sum_{i, j \text{ odd}} \frac{D_j D_i}{n_i n_j} \langle \tilde{i} \tilde{i} | v_{ee} | \tilde{j} \tilde{j} \rangle. \quad (59)$$

As already noticed in [52], the aesthetically appealing result (58) is puzzling, at least at first sight. All orbital energies are equal and equal to the total energy of the system. Only with NOs and their fractional OCNs does the simple additive form  $E = \sum_i \epsilon_i n_i$ —commonly known only from *noninteracting* systems—persist here for *interacting* systems.

### E. Two orbitals per spin

In our code that actually solves (35) we work on a numerical grid representing the discretized space variable  $x$  and the RNO index  $n = 1, 3, \dots, N_{\text{RNO}}$  (see Fig. 1). All sums over the RNO indices have to be terminated at some finite  $N_{\text{RNO}}$  in practice. Let us consider the simplest yet nontrivial case of two RNOs (per spin), i.e.,

$$n_1 = n_2 \neq 0, \quad n_3 = n_4 \neq 0, \quad n_i = 0 \quad \text{for } i > 4, \quad (60)$$

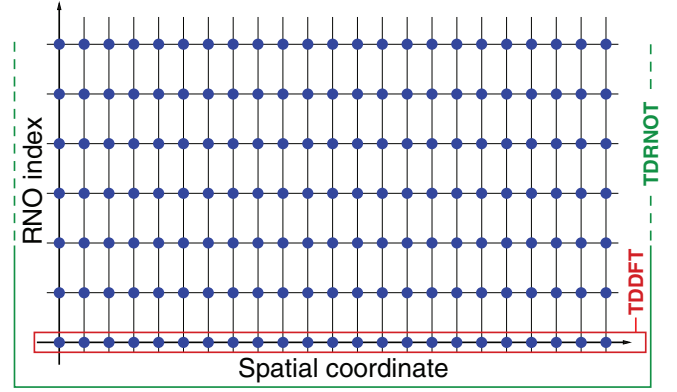


FIG. 1. (Color online) Sketch of the numerical grid. Each row corresponds to one of the RNOs. Horizontal flux of probability density represents motion in position space with the OCNs kept constant. Flux in vertical direction implies a change in the OCNs. Because we work with RNOs instead of NOs, the time evolution on this grid is unitary. In the two-electron spin-singlet case the restriction to a single RNO (per spin) corresponds to TDHF or TDDFT in EXA approximation (red). In time-dependent RNO theory (TDRNOT, green) more than one RNO is allowed.

which implies

$$\tilde{\phi}_1 = \tilde{\phi}_2, \quad \tilde{\phi}_3 = \tilde{\phi}_4, \quad \tilde{\phi}_i \equiv 0 \quad \text{for } i > 4. \quad (61)$$

As a single NO (per spin) is equivalent to TDHF (cf. Sec. II C), allowing for two RNOs per spin is just “one small step beyond TDHF.” However, we shall see below that two RNOs per spin are already enough to describe some of the correlated two-electron dynamics completely missed by TDHF (or TDKS in EXA). The relevant terms in (35) in this case are

$$\hat{\mathcal{H}}_1^0(x) = A_1 + \hat{\mathcal{K}}_1^0(x), \quad \hat{\mathcal{H}}_3^0(x) = A_3 + \hat{\mathcal{K}}_3^0(x), \quad (62)$$

$$\mathcal{H}_{13}^1(x) = B_{13} + \mathcal{K}_{13}^1(x), \quad \mathcal{H}_{31}^1(x) = \mathcal{H}_{13}^1(x)^*. \quad (63)$$

We find, making use of (34),

$$A_1 = -\frac{1}{n_1} \left[ \text{Re} \left( \langle \tilde{1} \tilde{1} | v_{ee} | \tilde{1} \tilde{1} \rangle + \frac{D_1 D_3^*}{n_1 n_3} \langle \tilde{3} \tilde{3} | v_{ee} | \tilde{1} \tilde{1} \rangle \right) + \langle \tilde{1} | \hat{h}_0 | \tilde{1} \rangle \right], \quad A_3 = A_1 [1 \leftrightarrow 3], \quad (64)$$

$$\hat{\mathcal{K}}_1^0(x) = \hat{h}_0(x) + \frac{\langle \tilde{1} | v_{ee} | \tilde{1} \rangle(x)}{n_1}, \quad \hat{\mathcal{K}}_3^0(x) = \hat{\mathcal{K}}_1^0(x) [1 \leftrightarrow 3], \quad (65)$$

$$B_{13} = \frac{1}{n_3 - n_1} \left( \frac{D_3 D_1^*}{n_1 n_3} \langle \tilde{1} \tilde{1} | v_{ee} | \tilde{1} \tilde{3} \rangle + \frac{\langle \tilde{3} \tilde{3} | v_{ee} | \tilde{1} \tilde{3} \rangle}{n_3} - \left[ \frac{D_1 D_3^*}{n_1 n_3} \langle \tilde{3} \tilde{3} | v_{ee} | \tilde{3} \tilde{1} \rangle + \frac{\langle \tilde{1} \tilde{1} | v_{ee} | \tilde{3} \tilde{1} \rangle}{n_1} \right]^* \right), \quad B_{31} = B_{13}^*, \quad (66)$$

$$\mathcal{K}_{13}^1(x) = \frac{D_3 D_1^*}{n_1 n_3} \langle \tilde{1} | v_{ee} | \tilde{3} \rangle(x), \quad \mathcal{K}_{31}^1(x) = \mathcal{K}_{13}^1(x)^*, \quad (67)$$

and the equation of motion has the simple structure,

$$i \partial_t \begin{pmatrix} \tilde{\phi}_1(x) \\ \tilde{\phi}_3(x) \end{pmatrix} = \begin{pmatrix} \hat{\mathcal{H}}_1^0(x) & \mathcal{H}_{13}^1(x) \\ \mathcal{H}_{31}^1(x) & \hat{\mathcal{H}}_3^0(x) \end{pmatrix} \begin{pmatrix} \tilde{\phi}_1(x) \\ \tilde{\phi}_3(x) \end{pmatrix}. \quad (68)$$

Here, the off-diagonal elements determine whether or not the OCNs are constant,

$$\dot{n}_1 = 2 \text{Im} \langle \tilde{1} | \mathcal{H}_{13}^1 | \tilde{3} \rangle, \quad \dot{n}_3 = 2 \text{Im} \langle \tilde{3} | \mathcal{H}_{13}^1 | \tilde{1} \rangle. \quad (69)$$

Furthermore, it is easy to show that the RNOs  $\tilde{\phi}_1$  and  $\tilde{\phi}_3$  stay orthogonal at all times.

### III. RESULTS AND DISCUSSION

The results in the following are obtained for the well-known model heliumlike atom introduced in [53] and used extensively ever since (see, e.g., [32,33,46,54]). In the spin-singlet configuration the full two-body TDSE reads

$$i \frac{\partial}{\partial t} \Psi(x_1 x_2; t) = \left[ \sum_{i=1}^2 \left( -\frac{1}{2} \frac{\partial^2}{\partial x_i^2} - \frac{2}{\sqrt{x_i^2 + 1}} - i A(t) \frac{\partial}{\partial x_i} \right) + \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}} \right] \Psi(x_1 x_2; t). \quad (70)$$

We employ the velocity gauge to couple an external field with vector potential  $A(t)$  in dipole approximation to the model atom (with the purely time-dependent term  $\sim A^2$  “transformed away”). The corresponding one-body Hamiltonian for the RNO equations reads accordingly

$$\hat{h}_0 = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - i A(t) \frac{\partial}{\partial x} - \frac{2}{\sqrt{x^2 + 1}} \quad (71)$$

and

$$v_{ee}(x_1 x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + 1}}. \quad (72)$$

For the real spin-singlet ground-state wave function of the He atom the geminal expansion coefficients  $D_i$  are

$$D_1 = \sqrt{n_1}, \quad D_i = -\sqrt{n_i} \quad \text{for } i = 3, 5, 7, \dots, \quad (73)$$

or, in terms of the phases introduced in Sec. IID,

$$\varphi_1 = 0, \quad \varphi_i = \pi \quad \text{for } i = 3, 5, 7, \dots. \quad (74)$$

A two-fermion system is the fortunate case where these phases are typically known for stationary configurations. However, it is in general not known how the  $D_i$  (or  $\varphi_i$ ) change in time with an external driver  $A(t)$  switched on (unless we solve the full two-electron TDSE and extract this information).

#### A. Ground-state RNOs

We applied imaginary-time propagation in combination with Gram-Schmidt orthogonalization to (68) with the  $D_i$  according (73) inserted in (64)–(67) in order to find the ground-state configuration for given OCN. A grid with  $N_x = 500$  spatial points and a resolution of  $\Delta x = 0.4$  was found to be sufficient for that purpose.

From Sec. IID we know that if we try all combinations

$$n_1 = 1.0 - y, \quad n_3 = y, \quad n_1 + n_3 = 1, \quad y \in [0, 1], \quad (75)$$

the ground-state configuration will be the one for which

$$\epsilon_1 = \epsilon_3 = \epsilon = E. \quad (76)$$

Figure 2 shows the orbital energies  $\epsilon_1$ ,  $\epsilon_3$  and the total energy  $E$  according (48) and (59), respectively, vs  $n_1$ . Condition (76) is fulfilled for

$$n_1 = 0.99127, \quad n_3 = 8.73 \times 10^{-3}, \quad (77)$$

with a total energy

$$E_{N_{\text{RNO}}=2} = -2.2366. \quad (78)$$

The two NOs are shown in Fig. 3.

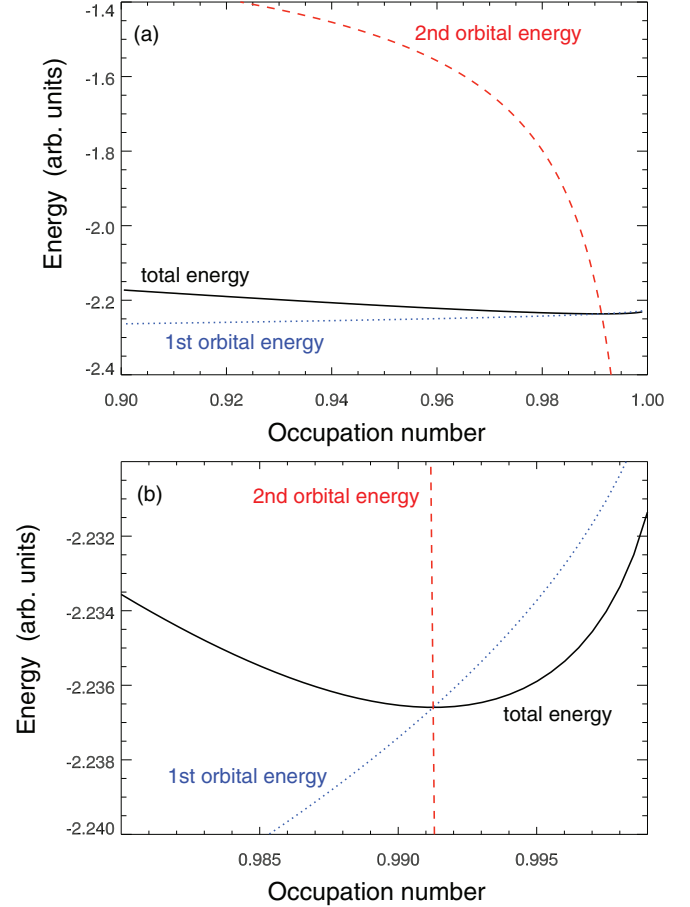


FIG. 2. (Color online) Orbital energies  $\epsilon_1$  (dotted blue),  $\epsilon_3$  (dashed red), and total energy  $E$  (solid black) vs the dominant OCN  $n_1$ . The physically relevant RNOs are obtained when the three curves cross [cf. (56) and (58)]. Panel (b) shows a zoom into the narrow  $n_1$  region where all energies cross in one point. The curves cross in the minimum of  $E$ .

From the full TDSE solution on a spatial  $500 \times 500$  grid, also with  $\Delta x = 0.4$ , we obtain the reference value for the ground-state energy,

$$E_{\text{TDSE}} = -2.2384 \quad (79)$$

and, via diagonalization of the 1RDM calculated from the two-body Schrödinger wave function, for the first five OCNs  $n_1 = 0.99096$ ,  $n_3 = 8.297 \times 10^{-3}$ ,  $n_5 = 7.063 \times 10^{-4}$ ,  $n_7 = 3.127 \times 10^{-5}$ ,  $n_9 = 7.392 \times 10^{-6}$ . The relative error in the total energy is thus only 0.08%. The HF ground-state energy of the system is  $E_{\text{HF}} = 2.2243$ , i.e., with 0.6% relative error.

The OCNs  $n_1$  and  $n_3$  we obtain for  $N_{\text{RNO}} = 2$  are slightly above the exact values because the two alone are already forced to sum up to unity.

The logarithmic ground-state contour plot of the full TDSE two-body electron density  $|\Psi(x_1 x_2; t)|^2$  shows characteristic kinks along the diagonal  $x_1 = x_2$  [see Fig. 6(a) below]. These kinks are not reproduced with only two RNOs since they are visible only on a probability density level governed by higher-order RNOs which have a much smaller OCN and which are spatially more extended. Nevertheless, we will see that two RNOs are already sufficient to describe, e.g., doubly excited

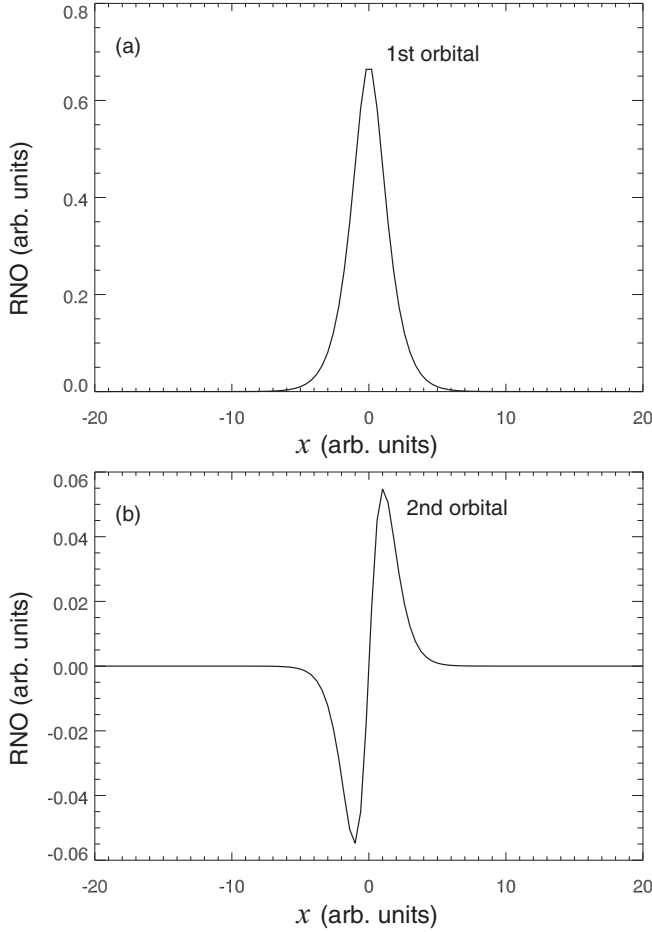


FIG. 3. Ground-state orbitals  $\tilde{\phi}_1$  (a) and  $\tilde{\phi}_3$  (b) for  $N_{\text{RNO}} = 2$ .

states and autoionization, not captured by (TD)DFT employing adiabatic xc potentials.

$$\underline{A}_1 = -\frac{1}{n_1} \left[ \langle \tilde{1}\tilde{1} | v_{ee} | \tilde{1}\tilde{1} \rangle - \frac{1}{\sqrt{n_1 n_3}} \langle \tilde{3}\tilde{3} | v_{ee} | \tilde{1}\tilde{1} \rangle + \langle \tilde{1} | \hat{h}_0 | \tilde{1} \rangle \right], \quad \underline{\mathcal{K}}_1^0(x) = \hat{h}_0(x) + \frac{\langle \tilde{1} | v_{ee} | \tilde{1} \rangle(x)}{n_1}, \quad (80)$$

$$\underline{B}_{13} = \frac{1}{n_3 - n_1} \left( \frac{\langle \tilde{3}\tilde{3} | v_{ee} | \tilde{1}\tilde{3} \rangle}{n_3} + \frac{\langle \tilde{3}\tilde{1} | v_{ee} | \tilde{3}\tilde{3} \rangle - \langle \tilde{1}\tilde{1} | v_{ee} | \tilde{1}\tilde{3} \rangle}{\sqrt{n_1 n_3}} - \frac{\langle \tilde{3}\tilde{1} | v_{ee} | \tilde{1}\tilde{1} \rangle}{n_1} \right), \quad \underline{\mathcal{K}}_{13}^1(x) = -\frac{1}{\sqrt{n_1 n_3}} \langle \tilde{1} | v_{ee} | \tilde{3} \rangle(x), \quad (81)$$

where we have used (73). The only remaining time dependence in the Hamiltonian in

$$i\partial_t \begin{pmatrix} \tilde{\phi}_1 \\ \tilde{\phi}_3 \end{pmatrix} = \begin{pmatrix} \underline{\mathcal{H}}_1^0 & \underline{\mathcal{H}}_{13}^1 \\ \underline{\mathcal{H}}_{31}^1 & \underline{\mathcal{H}}_3^0 \end{pmatrix} \begin{pmatrix} \tilde{\phi}_1 \\ \tilde{\phi}_3 \end{pmatrix} \quad (82)$$

then is in  $\hat{h}_0$  through the vector potential  $A(t)$ , i.e., only in the diagonal parts  $\underline{\mathcal{H}}_1^0$  and  $\underline{\mathcal{H}}_3^0$ .

Equations (82) and (80) and (81) can be easily generalized to more than two RNOs per spin. It is simple to prove that the sum of all OCNs is conserved,  $\partial_t \sum_i n_i = 0$ . With the frozen Hamiltonian the individual  $n_i$  may *not* stay constant, which is a good feature, as remarked on above. A drawback of

### B. “Frozen” Hamiltonian

The full nonlinear system (35) [and even its truncated form (68)] is numerically difficult to handle because of instabilities. The time evolution of the RNOs and the OCNs (i.e., the RNO norms) is extremely sensitive to the phases  $\varphi_i(t)$ . Although we apply an unconditionally stable (i.e., exactly unitary) propagation algorithm (including predictor-corrector steps) to our Schrödinger-like equation (68) (with a hermitian Hamiltonian), the individual OCNs  $n_i(t) = \langle \tilde{i}(t) | \tilde{i}(t) \rangle$ —while still adding up to unity—tend to develop an unphysical, rather erratic behavior after some time of propagation. Such a behavior is actually to be anticipated from Eqs. (69): the phases of the  $D_i$  and the phases of the RNOs determine the changes in the OCNs  $n_i$  which, in turn, are fed back into the Hamiltonian. One way to mitigate these instabilities is to make approximations to  $\tilde{\gamma}_{2,ijkl}$  that keep the OCNs constant. However, the change of the OCNs is often crucial to capture strongly driven, correlated, or resonant electron dynamics [33,46,47].

In TDKS calculations it is not uncommon to “freeze” the ground-state Kohn-Sham potential during time propagation, leading to the so-called “bare” Kohn-Sham response. The result can be compared to the full TDKS calculation. In this way one may identify the effect of the nonlinearity in the full Kohn-Sham potential. For instance, the peaks in the linear-response spectrum obtained from the bare Kohn-Sham Hamiltonian correspond to the (allowed) transitions between the eigenstates of this Hamiltonian. The nonlinearity in the full Kohn-Sham potential typically moves the peaks from the frozen transition energies towards the correct position (see [32] for the case of the model He atom studied here). We expect something similar for the differences in the linear-response spectrum calculated with the full, nonlinear Hamiltonian in (35) [or, for two RNOs, (68)] and the ground-state RNO-frozen Hamiltonian. Let us denote the ground-state RNOs, OCNs, etc. by the corresponding underlined quantities. Then, for two RNOs per spin, Eqs. (64)–(67) become

the frozen Hamiltonian, however, is that  $\partial_t \langle \tilde{i} | \tilde{n} \rangle = 0$  is not strictly fulfilled anymore. This means that different RNOs may not stay orthogonal during time propagation although, as eigenfunctions of a hermitian 1RDM, they should.

### C. Bare linear response

Figure 4 shows linear-response spectra for the He model system. All spectra were calculated by Fourier transforming the dipole after disturbance of the system with a minute electric-field kick, corresponding to a steplike vector potential.

The exact TDSE result shows the dominating series of peaks starting around a frequency  $\omega = 0.5$ . In the



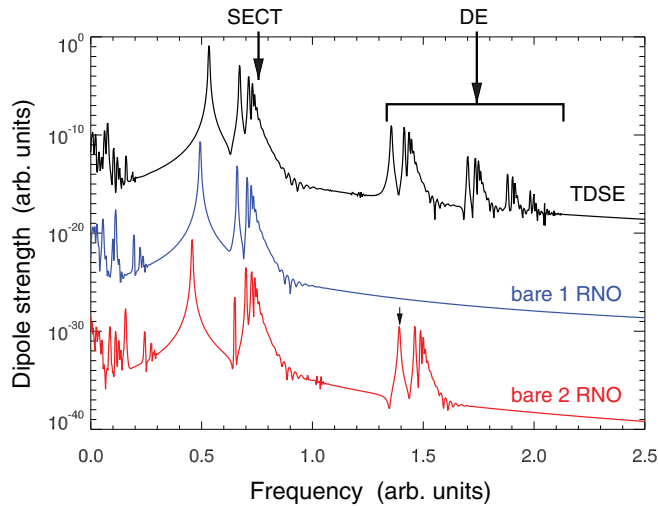


FIG. 4. (Color online) Linear response of the He model system obtained from the full TDSE (70) (upper, black, labeled “TDSE”), with a single RNO per spin, i.e., equivalent to bare TDHF or TDKS in EXA (center, blue, labeled “bare 1 RNO”), and two RNOs (lower, red, labeled “bare 2 RNO”). The single-electron continuum threshold is indicated by “SECT;” doubly excited series of peaks by “DE.” The little arrow indicates the first double-excitation peak in the bare two-RNO result, discussed in Sec. III D.

independent-electron picture, these peaks correspond to single-electron excitations: one electron stays in its ground state, the other one is excited to the first, second, etc. (dipole-allowed) state, up to the single-electron continuum threshold (SECT). Series of peaks corresponding to doubly excited states follow around  $\omega \simeq 1.3$  and greater. As in the “real” He atom, all double excitations are embedded in the single-ionization continuum and thus are autoionizing. Ultimately, with excitations of frequencies  $\omega > |E|$ , both electrons can be lifted into the two-electron continuum [55].

The linear-response spectrum obtained with just one RNO (per spin) is equivalent to the result of a bare TDHF (or TDKS-EXA) calculation [56]. One can show that doubly excited states are not even covered by full TDDFT (i.e., without frozen Kohn-Sham potential) as long as adiabatic exchange-correlation (xc) potentials are employed (see, e.g., [25]). With a frozen Hamiltonian and just a single RNO it is immediately clear that double excitations cannot exist. And indeed, the peaks corresponding to transitions to doubly excited states are absent for the “bare 1 RNO” result in Fig. 4. The single-excitation series is there but a bit redshifted as compared to the TDSE reference spectrum.

The first main result of this paper is that the first series of double-excitation peaks is present when Eq. (82) is solved. In order to reproduce double excitations in TDDFT one would have to use xc potentials with memory [38]. Even if useful potentials with memory were known they would very likely be computationally expensive. Instead, with our time-dependent RNO theory (TDRNOT) we cover double excitations even with a frozen Hamiltonian and just two RNOs. This is because we allow for more than one orbital per spin (or, in the single-particle picture, per particle), like in a configuration interaction calculation or in multiconfigurational Hartree-Fock. However, the advantage of TDRNOT over such

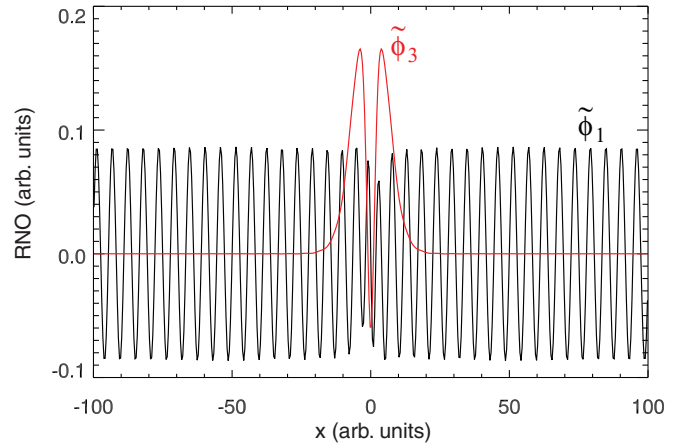


FIG. 5. (Color online) The two RNOs  $\tilde{\phi}_1(x)$  and  $\tilde{\phi}_3(x)$  of the autoionizing state indicated by the small vertical arrow in Fig. 4 for the bare two-RNO calculation.

methods is that the RNOs constitute automatically the most adequate time-dependent basis, as mentioned already in the Introduction. This is the reason why we get along with only two RNOs. Thanks to this small number of necessary RNOs we have only little computational overhead compared to the corresponding TDHF or TDKS-EXA simulation.

The single-excitation peaks in the bare two-RNO spectrum are even more redshifted compared to the TDSE than in the bare one-RNO result, while the peaks corresponding to double-excited states are slightly blueshifted. We have checked that with three RNOs the next series of double excitation peaks (seen in the TDSE result starting around  $\omega \simeq 1.7$ ) is also reproduced, although even more blueshifted. “Unfreezing” of the Hamiltonian should cure these shifts and improve the quantitative agreement between TDSE and TDRNOT results but, as mentioned above, we first have to overcome the instability problems before we can check this assertion.

#### D. Autoionization after excitation by a laser pulse

The small arrow in Fig. 4 indicates the lowest-lying transition to a doubly excited state in the bare TDRNOT He system employing two RNOs. The two RNOs for that particular state were calculated via diagonalization of the bare Hamiltonian in (82) on a grid with 500 spatial grid points. The result is depicted in Fig. 5. The dominating RNO  $\tilde{\phi}_1(x)$  has an OCN  $n_1 = 0.733$  and is delocalized, thus allowing for outgoing electron flux. Indeed, the spatial oscillations fit to the wave number  $k = \sqrt{2(\omega - I_p)} \simeq 1$  expected for the outgoing electron (with  $\omega \simeq 1.38$  the energy required to populate the autoionizing state and the ionization potential inferred from the SECT in Fig. 4,  $I_p \simeq 0.75$ ). The second RNO  $\tilde{\phi}_3(x)$  is localized close to the origin and has an OCN  $n_3 = 0.267$ . If one detunes from the autoionizing resonance the OCN of the delocalized NO increases. Hence, the characterizing feature of an autoionizing resonance (as compared to states in a “flat” continuum) is the relative increase of the occupation of localized NOs.

As an example for a TDRNOT calculation beyond linear response we have simulated the interaction of the model He atom with an  $N_{\text{cyc}} = 30$ -cycle  $\sin^2$ -shaped laser pulse of

frequency  $\omega$ , i.e.,

$$A(t) = \hat{A} \sin^2\left(\frac{\omega t}{2N_{\text{cyc}}}\right) \sin \omega t, \quad (83)$$

for  $0 < t < N_{\text{cyc}}T$  with  $T = 2\pi/\omega$ , and zero otherwise. The frequency in one calculation was chosen resonant with the transition to the first doubly excited, autoionizing state while in another run, for comparison, we tuned it off-resonant. In all cases the vector potential amplitude was  $\hat{A} = 0.01$ .

### 1. TDSE result in position space

Before showing the results obtained with the bare TDRNOT equation (82), let us illustrate the exact dynamics we observe by solving the full two-electron TDSE (70). The same model atom has been employed to study autoionization in the presence of an additional, optical laser pulse in [57].

For the off-resonant case we chose  $\omega = 1.25$ . In this case, we expect single-photon ionization while the laser is on and no ionization thereafter. In fact, this can be clearly inferred from the (logarithmically scaled) position space probability density plotted in Fig. 6(a) for time  $t = 255$ , i.e., well after the laser was off at  $30T = 151$ . Around the origin, the remaining ground-state density is visible. Around  $x_1 \simeq 180, x_2 = 0$  the laser-generated photoelectron wave packet is seen. It travels to the right with velocity (or wave number)  $k = \sqrt{2(\omega - I_p)} \simeq 1$ , where the ionization potential (for the TDSE calculation) is  $I_p = 0.751$ . Analogous wave packets travel in the  $-x_1$  and  $\pm x_2$  directions (not shown).

The frequency  $\omega = 1.36$  for the resonant case can be read off Fig. 4. Figure 6(b) shows the probability density, again at time  $t = 255$ . Because the frequency is higher than in (a), the photoelectron wave packet is faster and narrower ( $N_{\text{cyc}}$  was kept constant). The major qualitative differences compared to the off-resonant case is that (i) the system continues to ionize after the laser is off, as is seen from the trailing edge of probability density following the (directly) laser-generated photoelectron wave packet,

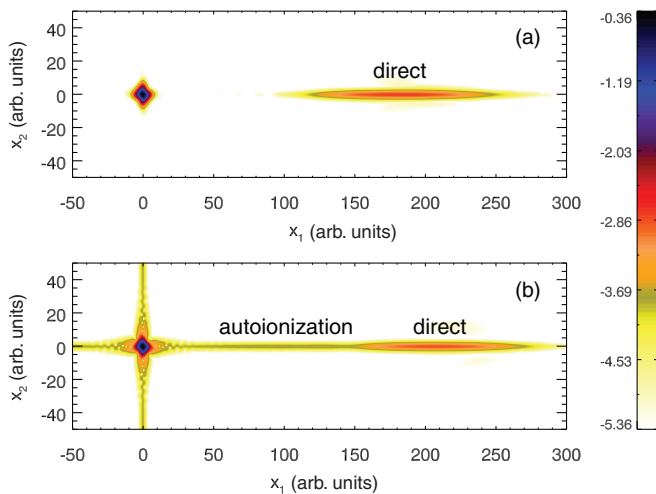


FIG. 6. (Color online) Logarithmic probability density (over five orders of magnitude) from (70) for a  $N_{\text{cyc}} = 30$ -cycle laser pulse with  $\hat{A} = 0.01$  at  $t = 255$  for the off-resonant case  $\omega = 1.25$  (a) and the resonant one  $\omega = 1.36$  (b). In (b), ionization continues after the laser pulse, as can be seen from the probability density trailing the (directly) laser-generated photoelectron wave packet.

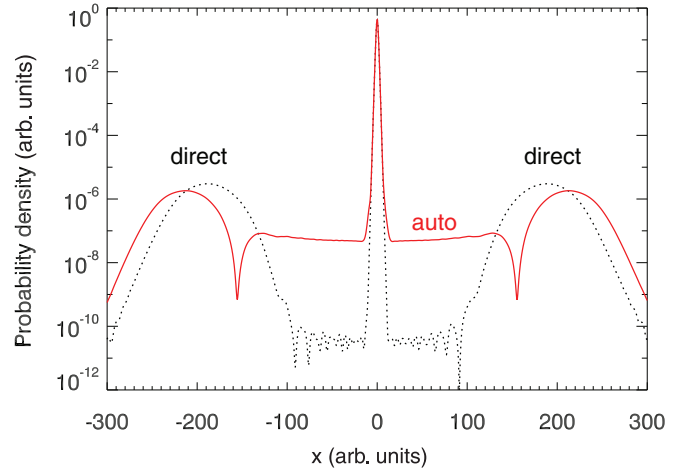


FIG. 7. (Color online) TDRNOT result corresponding to the TDSE two-electron density dynamics in Fig. 6. The off-resonant frequency used was  $\omega = 1.28$  (other parameters as in the TDSE runs), leading to the black, dotted density at  $t = 255$ . The resonant frequency  $\omega = 1.38$  yields the red, solid density.

wave packet, and (ii) the different structure in the probability density around the origin. The latter clearly shows that the system is not left in the ground state after the interaction with the laser pulse. Instead, it is in a superposition of ground and autoionizing state. Similar patterns are shown in [57].

### 2. Bare two-RNO result in position space

The probability density  $|\tilde{\phi}_1(x)|^2 + |\tilde{\phi}_3(x)|^2$  from the bare two-RNO simulation at  $t = 255$  is shown in Fig. 7. The laser frequency for the resonant excitation of the autoionizing state was tuned to the respective value  $\omega = 1.38$  indicated by an arrow in Fig. 4. For the nonresonant run  $\omega = 1.28$  was chosen. Again, left- and right-going photoelectron wave packets (with their maxima at the expected positions) are observed. In the case with autoionization (red, solid) a much higher probability density level between the origin and the wave packets is observed. This is the 1D analog of the TDSE density dynamics in the  $x_1, x_2$  plane in Fig. 6.

### 3. Momentum spectra

With autoionization involved, the electron spectra should display Fano line shapes [58]. Strictly speaking, one should calculate photoelectron spectra by projecting the final wave function at a time when the laser is off on field-free continuum eigenstates. When the final wave function is not available but only the RNOs, one can, in principle, rewrite the expectation value of the corresponding spectral projection operator in terms of the 2DM  $\gamma_2$  or the coefficients  $D_i$ . The latter need to be approximated anyway in the general TDRNOT approach. Hence, there is no conceptual problem in calculating any observable for systems with two-body interactions because the knowledge of  $\gamma_2$  suffices. Note that in TDDFT it is not clear how to calculate photoelectron spectra in a rigorous way because the density functional for this observable is unknown [59].

Projection on field-free continuum states is computationally expensive. Hence, it is quite common in practice to project out

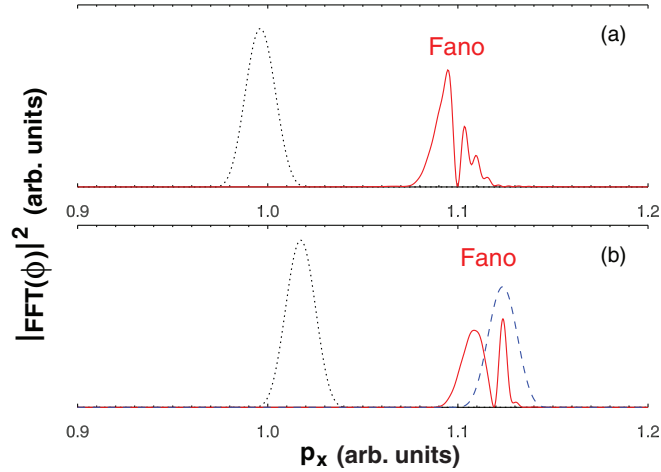


FIG. 8. (Color online) Linearly scaled photoelectron momentum spectra obtained by Fourier transforming (FFT) the outgoing part of the TDSE wave function (a) and RNO (b) for a  $N_{\text{cyc}} = 100$  laser pulse of the form (83) with  $\hat{A} = 0.01$ . The same resonant (solid, red) and off-resonant (dotted, black) frequencies as in Figs. 6 and 7 were chosen. The spectra were obtained at times  $t = 750$ . Fano profiles are seen in the TDSE result at resonance and the TDRNOT result at resonance when two RNOs are employed (red). In panel (b) the result for a single NO and  $\omega = 1.38$  (dashed, blue) is also plotted, showing no Fano profile.

the most populated bound states and Fourier transform the “rest” in order to obtain momentum spectra. Alternatively, one may filter out the region around the origin. While not being a rigorous way to calculate photoelectron spectra, the method yields sufficiently accurate spectra for our purposes. Hence, we pursued the same strategy and Fourier transformed the outgoing part of the wave function. In this way we obtain the momentum spectra shown in Fig. 8.

The TDSE results for the modulus square of the Fourier transform (integrated over  $p_{x_2}$ ) are presented in Fig. 8(a). The off-resonant excitation by an  $N_{\text{cyc}} = 100$  laser pulse of the form (83) (the same frequency  $\omega = 1.25$  and field amplitude as in Fig. 6) leads to a peak close to momentum  $p_x = 1$ , as expected. The resonant excitation leads to a Fano “kink” in the photoelectron peak at  $p_x \simeq 1.1$ .

Figure 8(b) shows the bare two-RNO TDRNOT results. The second main result of this work—after the existence of doubly excited states—is that our approach also yields a resonance peak with a Fano kink (solid, red). Although the detailed shape of the Fano resonance differs from the TDSE result it is remarkable that it is present at all. As emphasized already, autoionizing states are not captured by a TDHF or TDKS calculation (with adiabatic xc potentials). As a consequence, Fano profiles will not be present there either. The black, dotted peak in Fig. 8(b) is the result for the off-resonant frequency. The dashed blue peak is obtained for  $\omega = 1.38$  but with one NO only (equivalent to the bare TDHF result). As there are no

doubly excited states with one NO, there is no autoionization and thus no Fano profile.

#### IV. CONCLUSION AND OUTLOOK

We have introduced time-dependent renormalized natural orbital theory (TDRNOT) and tested it with a numerically exactly solvable model helium atom. The main result is that even with only two renormalized natural orbitals (RNOs) and the bare (i.e., “frozen”) effective ground-state Hamiltonian we observe correlation signatures impossible to capture with time-dependent density functional theory (TDDFT) using adiabatic exchange-correlation potentials, namely (i) excitation of doubly excited states in the linear-response spectrum and—beyond linear response—(ii) autoionization and Fano profiles in the photoelectron spectra. The numerical effort scales with the number of RNOs cubed but only linearly with the number of spatial grid points required for one particle. While in TDDFT exchange-correlation potentials with memory are required to capture doubly excited states, the effective Hamiltonian in TDRNOT is local in time. Moreover, the problem in TDDFT concerning density functionals for observables that are not explicitly known in terms of the single-particle density is removed.

Future work will be devoted to other two-electron systems in laser fields (in full dimensionality, spin triplet,  $\text{H}_2$ ), resonant interactions, and three-electron model systems that are still numerically exactly solvable. In full dimensionality, each RNO will be expanded in spherical harmonics and with the radial coordinate discretized as in this work. Then, one may apply analogs of the central field approximation for ground-state calculations and a multipole expansion of the effective Hamiltonian for time-dependent simulations. In the spin-triplet case the algebraic structure of the two-body density matrix (or two-electron wave function) expansion is different from the spin singlet but otherwise the approach is the same. The same holds for  $\text{H}_2$ . Three-electron systems such as the lithium atom in intense laser fields is of interest as it is the simplest system with “inner” electrons in a closed shell. The time-dependent Schrödinger equation of one-dimensional model Li atoms in intense laser fields is still possible to solve exactly [60] and thus may serve as a benchmark for our method. Another research direction will be the development of density matrix functionals that allow one to go beyond the bare TDRNOT without unleashing instabilities in the RNO equation of motion.

#### ACKNOWLEDGMENT

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#### APPENDIX A: DERIVATION OF EOM (13)

Inserting (6) and (9) into (5) yields (suppressing all time arguments)

$$\begin{aligned}
 & -i \sum_k [\partial_t n_k] \phi_k^*(1') \phi_k(1) - i \sum_k n_k [\partial_t \phi_k^*(1')] \phi_k(1) - i \sum_k n_k \phi_k^*(1') [\partial_t \phi_k(1)] \\
 & = [\hat{h}_0(1') - \hat{h}_0(1)] \sum_k n_k \phi_k^*(1') \phi_k(1) + 2 \int d2 \{v_{ee}(|1' - 2|) - v_{ee}(|1 - 2|)\} \sum_{ijkl} \gamma_{2,ijkl} \phi_i(1) \phi_j(2) \phi_k^*(1') \phi_l^*(2). \quad (\text{A1})
 \end{aligned}$$

Because the NOs form a complete basis we may introduce time-dependent coefficients  $\alpha_{km}(t)$  [10] such that

$$i \partial_t \phi_k(t) = \alpha_{kk}(t) \phi_k(t) + \sum_{m \neq k} \alpha_{km}(t) \phi_m(t). \quad (\text{A2})$$

Here we drop the argument 1 as the equation holds for all position and spin degrees of freedom. With the transformation

$$\phi_k(t) = e^{-i \int^t \alpha_{kk}(t') dt'} \phi'_k(t) \quad (\text{A3})$$

[where  $\alpha_{kk}$  is real because of  $\alpha_{km}(t) = \alpha_{mk}^*(t)$ ] we transform away the diagonal part of  $\alpha_{km}$  and obtain

$$i \partial_t \phi'_k(t) = \sum_{m \neq k} \alpha'_{km}(t) \phi'_m(t), \quad \alpha'_{km}(t) = \alpha_{km}(t) e^{-i \int^t [\alpha_{mm}(t') - \alpha_{kk}(t')] dt'}. \quad (\text{A4})$$

$\alpha'_{km}$  constitutes another hermitian matrix. The NOs are defined as the eigenfunctions of the hermitian 1RDM. We have the freedom to choose the phase in such a way that (A4) holds. This is the analog of switching to the interaction picture, but now for a nonlinear Hamiltonian. Dropping the primes,  $\phi' \rightarrow \phi$ ,  $\alpha' \rightarrow \alpha$ , we have for (A1)

$$\begin{aligned} & -i \sum_k [\partial_t n_k] \phi_k^*(1) \phi_k(1) + \sum_{k, m \neq k} n_k \alpha_{km}^* \phi_m^*(1) \phi_k(1) - \sum_{k, m \neq k} n_k \phi_k^*(1) \alpha_{km} \phi_m(1) \\ & = [\hat{h}_0(1') - \hat{h}_0(1)] \sum_k n_k \phi_k^*(1) \phi_k(1) + 2 \int d2 \{v_{ee}(|1' - 2|) - v_{ee}(|1 - 2|)\} \sum_{ijkl} \gamma_{2,ijkl} \phi_i(1) \phi_j(2) \phi_k^*(1) \phi_l^*(2). \end{aligned} \quad (\text{A5})$$

Multiplying by  $\phi_n(1')$ ,  $\phi_p^*(1)$ , and integrating over 1 and 1' gives

$$-i \dot{n}_n \delta_{np} + n_p \alpha_{pn}^* - n_n \alpha_{np} = (n_p - n_n) \langle p | \hat{h}_0 | n \rangle + 2 \sum_{jkl} \{ \gamma_{2,pjkl} \langle kl | v_{ee} | nj \rangle - [\gamma_{2,njkl} \langle kl | v_{ee} | pj \rangle]^* \}. \quad (\text{A6})$$

For  $n = p$  we obtain (17)

$$\dot{n}_n = -4 \text{Im} \sum_{jkl} \gamma_{2,njkl} \langle kl | v_{ee} | nj \rangle. \quad (\text{A7})$$

For  $n \neq p$  we have

$$\alpha_{np}(n_p - n_n) = (n_p - n_n) \langle p | \hat{h}_0 | n \rangle + 2 \sum_{jkl} \{ \gamma_{2,pjkl} \langle kl | v_{ee} | nj \rangle - [\gamma_{2,njkl} \langle kl | v_{ee} | pj \rangle]^* \}. \quad (\text{A8})$$

If  $n_p \neq n_n$  we can divide by  $n_p - n_n$ , which gives with (A4)

$$i \partial_t \phi_n = \sum_{p \neq n} \left( \langle p | \hat{h}_0 | n \rangle + \frac{2}{n_p - n_n} \sum_{jkl} \{ \gamma_{2,pjkl} \langle kl | v_{ee} | nj \rangle - [\gamma_{2,njkl} \langle kl | v_{ee} | pj \rangle]^* \} \right) \phi_p. \quad (\text{A9})$$

Equations (A9) and (A6) are EOMs for NOs and OCNs, respectively, but not useful for our purposes because truncating them to a small number of NOs would yield extremely poor results [61]. Instead, it is more suitable to seek an EOM of the form of Eq. (12),  $i \partial_t \Phi(1) = \hat{\mathcal{H}}(1) \Phi(1)$ , where  $\Phi(1, t)$  is a vector of NOs  $\phi_k(1, t)$  and  $\hat{\mathcal{H}}$  acts in NO and position-spin space (see Fig. 1) instead of only in NO space as in (A9). Multiplying (A1) by  $\phi_n(1')$  and integrating-out only 1' (but not 1) leads to

$$\begin{aligned} i \partial_t \phi_n(1) &= \frac{4i}{n_n} \left\{ \text{Im} \sum_{jkl} \gamma_{2,njkl} \langle kl | v_{ee} | nj \rangle \right\} \phi_n(1) - \langle n | \hat{h}_0 | n \rangle \phi_n(1) \\ &+ \sum_{k \neq n} \frac{2n_k / n_n}{n_k - n_n} \sum_{jpl} \{ \gamma_{2,kjpl} \langle pl | v_{ee} | nj \rangle - [\gamma_{2,njpl} \langle pl | v_{ee} | kj \rangle]^* \} \phi_k(1) - \frac{2}{n_n} \sum_{kjpl} \gamma_{2,kjpl} \langle pl | v_{ee} | nj \rangle \phi_k(1) \\ &+ \hat{h}_0(1) \phi_n(1) + \frac{2}{n_n} \sum_{kjl} \gamma_{2,kjnl} \langle l | v_{ee} | j \rangle(1) \phi_k(1). \end{aligned} \quad (\text{A10})$$

In the first line on the right-hand side there are purely time-dependent coefficients in front of  $\phi_n(1)$ . This part of the total Hamiltonian  $\hat{\mathcal{H}}(1)$  is diagonal in both NO-index and position-spin space. In the second line we have the terms corresponding to the NO-index off-diagonal part of the

Hamiltonian. In the third line the first term does the ‘‘usual’’ coupling in position (spin) space due to the single-particle Hamiltonian  $\hat{h}_0$ . This term is diagonal in NO space. The second term in the third line couples the NOs through space-dependent (though multiplicative) coefficients.

It is simple to rewrite the EOM (A10) in terms of the RNOs (10). Using (A7) and (14), the result (13) is obtained.

#### APPENDIX B: CONNECTION BETWEEN $\gamma_{2,njkl}$ AND $D_i$

For the 2DM in the two-electron spin-singlet case we find, using (22),

$$\gamma_2(12, 1'2') = \Phi(x_1 x_2) \Phi^*(x'_1 x'_2) \frac{1}{2} (\delta_{\sigma_1 + \delta_{\sigma_2 -}} - \delta_{\sigma_1 - \delta_{\sigma_2 +}}) \times (\delta_{\sigma'_1 + \delta_{\sigma'_2 -}} - \delta_{\sigma'_1 - \delta_{\sigma'_2 +}}), \quad (\text{B1})$$

and with (9)

$$\begin{aligned} \Phi(x_1 x_2) \Phi^*(x'_1 x'_2) \frac{1}{2} (\delta_{\sigma_1 + \delta_{\sigma_2 -}} - \delta_{\sigma_1 - \delta_{\sigma_2 +}}) (\delta_{\sigma'_1 + \delta_{\sigma'_2 -}} - \delta_{\sigma'_1 - \delta_{\sigma'_2 +}}) \\ = \sum_{ijkl} \gamma_{2,ijkl} \phi_i(x_1) \delta_{\sigma_i \sigma_j} \phi_j(x_2) \delta_{\sigma_2 \sigma_j} \phi_k^*(x'_1) \delta_{\sigma'_i \sigma'_k} \phi_l^*(x'_2) \delta_{\sigma'_2 \sigma'_l}. \end{aligned} \quad (\text{B2})$$

Multiplication by NOs and integration allows us to solve for the  $\gamma_2$  expansion coefficients,

$$\gamma_{2,mnop} = \frac{1}{2} (\delta_{\sigma_o + \delta_{\sigma_p -}} - \delta_{\sigma_o - \delta_{\sigma_p +}}) \times (\delta_{\sigma_m + \delta_{\sigma_n -}} - \delta_{\sigma_m - \delta_{\sigma_n +}}) \gamma_{2,mnop}^{(x)} \quad (\text{B3})$$

with the spatial part

$$\begin{aligned} \gamma_{2,mnop}^{(x)} &= \int dx_1 \int dx_2 \int dx'_1 \int dx'_2 \phi_n^*(x_2) \phi_m^*(x_1) \\ &\times \Phi(x_1 x_2) \Phi^*(x'_1 x'_2) \phi_o(x'_1) \phi_p(x'_2) \\ &= \int dx_1 \int dx_2 \int dx'_1 \int dx'_2 \phi_n^*(x_2) \phi_m^*(x_1) \\ &\times \sum_{i \text{ odd}} D_i \phi_i(x_1) \phi_i(x_2) \\ &\times \sum_{j \text{ odd}} D_j^* \phi_j(x'_1) \phi_j(x'_2) \phi_o(x'_1) \phi_p(x'_2). \end{aligned} \quad (\text{B4})$$

Now, one must not forget that, e.g., not only  $m = i$  contributes but also  $m = i + 1$  because  $\phi_i = \phi_{i+1}$  for  $i$  odd. Hence

$$\gamma_{2,mnop}^{(x)} = (\delta_{m,i} + \delta_{m,i+1}) (\delta_{n,i} + \delta_{n,i+1}) D_i D_j^* (\delta_{o,j} + \delta_{o,j+1}) \times (\delta_{p,j} + \delta_{p,j+1}) \quad \text{for } i, j \text{ odd} \quad (\text{B5})$$

TABLE I. Nonvanishing  $\gamma_{2,mnop}$  in the case of two NOs per spin in the two-electron spin-singlet case and for approximations of the form (18).

$m$	$n$	$o$	$p$	$\gamma_{2,mnop}$	$\gamma_{2,mnop}^{(\text{approx})}$
1	2	1	2	$\frac{1}{2} D_1 ^2 = n_1/2$	$f_{1212}$
1	2	2	1	$-\frac{1}{2} D_1 ^2 = -n_1/2$	$-g_{1221}$
1	2	3	4	$\frac{1}{2}D_1 D_3^* = \frac{1}{2}\sqrt{n_1 n_3} e^{i\varphi}$	0
1	2	4	3	$-\frac{1}{2}D_1 D_3^* = -\frac{1}{2}\sqrt{n_1 n_3} e^{i\varphi}$	0
2	1	1	2	$-\frac{1}{2} D_1 ^2 = -n_1/2$	$-g_{2112}$
2	1	2	1	$\frac{1}{2} D_1 ^2 = n_1/2$	$f_{2121}$
2	1	3	4	$-\frac{1}{2}D_1 D_3^* = -\frac{1}{2}\sqrt{n_1 n_3} e^{i\varphi}$	0
2	1	4	3	$\frac{1}{2}D_1 D_3^* = \frac{1}{2}\sqrt{n_1 n_3} e^{i\varphi}$	0
3	4	1	2	$\frac{1}{2}D_3 D_1^* = \frac{1}{2}\sqrt{n_1 n_3} e^{-i\varphi}$	0
3	4	2	1	$-\frac{1}{2}D_3 D_1^* = -\frac{1}{2}\sqrt{n_1 n_3} e^{-i\varphi}$	0
3	4	3	4	$\frac{1}{2} D_3 ^2 = n_3/2$	$f_{3434}$
3	4	4	3	$-\frac{1}{2} D_3 ^2 = -n_3/2$	$-g_{3443}$
4	3	1	2	$-\frac{1}{2}D_3 D_1^* = -\frac{1}{2}\sqrt{n_1 n_3} e^{-i\varphi}$	0
4	3	2	1	$\frac{1}{2}D_3 D_1^* = \frac{1}{2}\sqrt{n_1 n_3} e^{-i\varphi}$	0
4	3	3	4	$-\frac{1}{2} D_3 ^2 = -n_3/2$	$-g_{4334}$
4	3	4	3	$\frac{1}{2} D_3 ^2 = n_3/2$	$f_{4343}$

and thus

$$\begin{aligned} \gamma_{2,mnop} &= \frac{1}{2} (\delta_{\sigma_o + \delta_{\sigma_p -}} - \delta_{\sigma_o - \delta_{\sigma_p +}}) (\delta_{\sigma_m + \delta_{\sigma_n -}} - \delta_{\sigma_m - \delta_{\sigma_n +}}) \\ &\times (\delta_{m,i} + \delta_{m,i+1}) (\delta_{n,i} + \delta_{n,i+1}) D_i D_j^* (\delta_{o,j} + \delta_{o,j+1}) \\ &\times (\delta_{p,j} + \delta_{p,j+1}) \quad \text{for } i, j \text{ odd}. \end{aligned} \quad (\text{B6})$$

Because of the spin part and our indexing (odd index  $\leftrightarrow$  spin up, even index  $\leftrightarrow$  spin down, see Sec. II B), for  $\gamma_{2,mnop}$  not to vanish the index pair  $(o, p)$  must be (even, odd) or (odd, even). The same holds for the index pair  $(m, n)$ .

In the case of two NOs per spin this leads to the nonvanishing  $\gamma_{2,mnop}$  summarized in Table I. We not only have the general property  $\gamma_{2,mnop} = \gamma_{2,opmn}^*$  here but also  $\gamma_{2,mnop} = -\gamma_{2,mnpo} = -\gamma_{2,nmop} = \gamma_{2,nmpo}$ . We also show the results for typical approximations of the form (18), which give erroneously zeros for ‘‘cross-block’’ elements like  $mnop = 1234$  or  $3421$  while they may give erroneously diagonal contributions, e.g.,  $f_{1111} - g_{1111}$  unless  $f_{mnop} = g_{mnop}$ , as in Hartree-Fock.

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