Approaches to Time-Dependent Multicomponent Dynamics

Chirag Jhala* and Manfred Lein
Institut für Physik, Universität Kassel,
Heinrich-Plett-Straße 40, D-34132 Kassel, Germany.

Abstract

Multicomponent density functional theory (MCDFT) for molecules treats electrons and nuclei on the same footing. Since practical functionals for time-dependent MCDFT are hardly available, we study an H_2^+ model system, where we can calculate the exact Kohn-Sham (KS) potentials by solving the time-dependent Schrödinger equation and inverting the time-dependent KS equations. As an alternative approach, we propose the application of the multi-configuration time-dependent Hartree method to electrons and nuclei.

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*Electronic address: `Chirag.Jhala@physik.uni-kassel.de`

I. DENSITY FUNCTIONAL THEORY: FROM 1964 TILL TODAY

In their seminal paper on density functional theory (DFT), Hohenberg and Kohn [1] proved that every ground-state observable of a quantum system composed of identical interacting particles is determined by the density of the system alone. The Runge-Gross theorem is an equivalent statement for the time-dependent situation [2]. The density of an interacting system can be calculated in terms of the density of an auxiliary system of non-interacting particles [3]. Such an auxiliary system is governed by a local effective potential termed as the Kohn-Sham (KS) potential [3]. The KS potential contains all the many-body effects of the system. A suitable approximation is needed for the KS potential.

In the past two decades DFT has been used to provide qualitative description of atoms in high intensity fields. For an accurate description of molecules in high-intensity fields, the additional nuclear degrees of freedom must be taken into account. Classical description of the nuclei or using the Born-Oppenheimer (BO) approximation cannot explain the complex interplay between the electronic and nuclear motion. A proper treatment is desired which treats the dynamics of electrons and nuclei quantum mechanically and on equal footing. To address this issue in the spirit of DFT, *multicomponent* DFT (MCDFT) has been proposed [4, 5].

II. MULTICOMPONENT DENSITY FUNCTIONAL THEORY: AN OVERVIEW

The Hamiltonian for the complete system of N_e electrons and N_n nuclei reads

$$\widehat{H}(t) = \widehat{T}_\mathrm{n}(\underline{\mathbf{R}}) + \widehat{T}_\mathrm{e}(\underline{\mathbf{r}}) + \widehat{W}_\mathrm{en}(\underline{\mathbf{r}},\underline{\mathbf{R}}) + \widehat{W}_\mathrm{nn}(\underline{\mathbf{R}}) + \widehat{W}_\mathrm{ee}(\underline{\mathbf{r}}) + \widehat{V}_\mathrm{ext,n}(\underline{\mathbf{R}},t) + \widehat{V}_\mathrm{ext,e}(\underline{\mathbf{r}},t) \tag{1}$$

$$\widehat{T}_\mathrm{n} = \sum_{\nu=1}^{N_\mathrm{n}} -\frac{\nabla_\nu^2}{2M_\nu} \;;\; \widehat{T}_\mathrm{e} = \sum_{j=1}^{N_\mathrm{e}} -\frac{\nabla_j^2}{2m} \tag{2}$$

$$\widehat{W}_\mathrm{nn} = \frac{1}{2}\sum_{\nu\neq\mu}^{N_\mathrm{n}} \frac{Z_\nu Z_\mu}{|\mathbf{R}_\nu - \mathbf{R}_\mu|} \;;\; \widehat{W}_\mathrm{ee} = \frac{1}{2}\sum_{j\neq k}^{N_\mathrm{e}} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} \tag{3}$$

$$\widehat{W}_\mathrm{en} = -\sum_{j=1}^{N_\mathrm{e}}\sum_{\nu=1}^{N_\mathrm{n}} \frac{Z_\nu}{|\mathbf{r}_\mathrm{j} - \mathbf{R}_\nu|} \tag{4}$$

$$\widehat{V}_\mathrm{ext,n} = \sum_{\nu=1}^{N_\mathrm{n}} V_\mathrm{ext,n}(\mathbf{R}_\nu,t) \;;\; \widehat{V}_\mathrm{ext,e} = \sum_{j=1}^{N_\mathrm{e}} V_\mathrm{ext,e}(\mathbf{r}_j,t) \;. \tag{5}$$

Equation (2) denotes the kinetic-energy operators of the nuclei and electrons respectively. Equations (3) and (4) represent the interparticle Coulomb interactions. Equation (5) represents all possible external potentials acting on the system. All the electronic coordinates are labeled by $\{\mathbf{r}_j\} \equiv \underline{\mathbf{r}}$ and the nuclear coordinates by $\{\mathbf{R}_\nu\} \equiv \underline{\mathbf{R}}$. The above Hamiltonian provides a quantum mechanical description of all degrees of freedom. Atomic units are employed throughout this work.

A. Coordinate transformation

First the laboratory coordinates of the electron are transformed to coordinates defined reltive to the nuclear center of mass (CM). Then these relative coordinates are rotated into the body-fixed internal coordinates $\underline{\mathbf{r}}'$. After this transformation the Hamiltonian reads [5]

$$\widehat{H}(t) = \widehat{T}_{\mathrm{n}}(\underline{\mathbf{R}}) + \widehat{T}_{\mathrm{e}}(\underline{\mathbf{r}}') + \widehat{T}_{\mathrm{MPC}}(\underline{\mathbf{r}}', \underline{\mathbf{R}}) + \widehat{W}_{\mathrm{nn}}(\underline{\mathbf{R}}) + \widehat{W}_{\mathrm{ee}}(\underline{\mathbf{r}}') + \widehat{W}_{\mathrm{en}}(\underline{\mathbf{r}}', \underline{\mathbf{R}}) + \widehat{V}_{\mathrm{ext}}(\underline{\mathbf{r}}', \underline{\mathbf{R}}, t) \ . \tag{6}$$

The nuclear coordinates have been left unchanged. $\widehat{T}_{\mathrm{MPC}}$ denotes mass-polarization and coriolis terms.

B. Defining the Densities

The basic requirements for the electronic density ρ and nuclear density Γ are the following: 1) The basic electronic density should be a single-particle quantity. 2) The densities should be characteristic for the internal properties of the system. 3) The treatment of the nuclear degrees of freedom should allow for appropriate description of various situations such as photodissociation. A set of densities which meets these requirements is given by

$$\Gamma(\underline{\mathbf{R}}, t) = \int d\underline{\mathbf{r}}' |\psi(\underline{\mathbf{R}}, \underline{\mathbf{r}}', t)|^2 \ , \tag{7}$$

$$\rho(\mathbf{r}', t) = N_{\mathrm{e}} \int d\underline{\mathbf{R}} \int d\mathbf{r}_2' \cdots d\mathbf{r}_{N_{\mathrm{e}}}' |\psi(\underline{\mathbf{R}}, \{\mathbf{r}', \mathbf{r}_2', \cdots \mathbf{r}_{N_{\mathrm{e}}}'\}, t)|^2 \ . \tag{8}$$

C. The Runge-Gross theorem for multicomponent system

In contrast to the ground-state formalism, the time-dependent MCDFT scheme is based on the time-dependent Schrödinger equation $i\frac{\partial\psi(\mathrm{t})}{\partial \mathrm{t}} = \widehat{\mathrm{H}}(\mathrm{t})\psi(\mathrm{t})$.

We write now the Hamiltonian in the form

$$\widehat{H}(t) = \widehat{T}_{\mathrm{n}}(\underline{\mathbf{R}}) + \widehat{T}_{\mathrm{e}}(\underline{\mathbf{r}}) + \widehat{T}_{\mathrm{MPC}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}) + \widehat{W}_{\mathrm{ee}}(\underline{\mathbf{r}}) + \widehat{W}_{\mathrm{en}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}) + \widehat{V}_{\mathrm{ext}}(\underline{\mathbf{r}}, \underline{\mathbf{R}}, t) + \widehat{V}_{\mathrm{e}}(\underline{\mathbf{r}}, t) + \widehat{V}_{\mathrm{n}}(\underline{\mathbf{R}}, t) \ , \tag{9}$$

where we have dropped the primes of the electron coordinates for the ease of notation and we have introduced two auxiliary potentials

$$\widehat{V}_{\mathrm{e}}(\underline{\mathbf{r}}, t) \ = \ \sum_{j=1}^{N_{\mathrm{e}}} V_{\mathrm{e}}(\mathbf{r}_{\mathbf{j}}, t) \ , \tag{10}$$

$$\widehat{V}_{\mathrm{n}}(\underline{\mathbf{R}}, t) \ = \ V_{\mathrm{n}}(\underline{\mathbf{R}}, t) \ . \tag{11}$$

On the basis of the densities given in Equations (7) and (8), the Runge-Gross theorem which is the time-dependent analog of the Hohenberg-Kohn theorem can be proved for multicomponent systems. Considering the time evolution of a molecule from an arbitrary initial state $\psi(t_0) = \psi_0$ under the influence of different external potentials, the Schrödinger equation defines a map which uniquely assigns the many-body wave function to the set of external potentials:

$$\mathcal{A} : \{V_{\mathrm{n}}(\underline{\mathbf{R}}, t), V_{\mathrm{e}}(\mathbf{r}, t)\} \longrightarrow \psi(t). \tag{12}$$

Employing the densities of Equations (7) and (8), a second map is established between many body wave function and the set of time-dependent densities,

$$\mathcal{B} : \psi(t) \longrightarrow \{\Gamma(\underline{\mathbf{R}}, t), \rho(\mathbf{r}, t)\} \ . \tag{13}$$

The main issue here is the proof of the invertibility of the combined map $\mathcal{G} \equiv \mathcal{A} \circ \mathcal{B}$:

$$\mathcal{G} : \{V_{\mathrm{n}}(\underline{\mathbf{R}}, t), V_{\mathrm{e}}(\mathbf{r}, t)\} \longrightarrow \{\Gamma(\underline{\mathbf{R}}, t), \rho(\mathbf{r}, t)\} \ . \tag{14}$$

In [4], the Runge-Gross theorem has been extended to multicomponent systems. Applied to our case, the statement is the following. Two sets of densities $\{\Gamma'(\underline{\mathbf{R}}, \mathrm{t}), \rho'(\mathbf{r}, \mathrm{t})\}$ and $\{\Gamma(\underline{\mathbf{R}}, \mathrm{t}), \rho(\mathbf{r}, \mathrm{t})\}$, evolving from the same initial state ψ_0 under the influence of two sets of potentials $\{\mathrm{V}'_{\mathrm{n}}(\underline{\mathbf{R}}, \mathrm{t}), \mathrm{V}'_{\mathrm{e}}(\mathbf{r}, \mathrm{t})\}$ and $\{\mathrm{V}_{\mathrm{n}}(\underline{\mathbf{R}}, \mathrm{t}), \mathrm{V}_{\mathrm{e}}(\mathbf{r}, \mathrm{t})\}$ differ infinitesimally after t_0, provided at least one component of the potentials differs by more than a time-dependent function,

$$\begin{gathered} V_{\mathrm{n}}(\underline{\mathbf{R}}, t) \neq V'_{\mathrm{n}}(\underline{\mathbf{R}}, t) + C(t) \\ \vee \\ V_{\mathrm{e}}(\mathbf{r}, t) \neq V'_{\mathrm{e}}(\mathbf{r}, t) \ + \ c(t) \ . \end{gathered} \tag{15}$$

Consequently, the rigorous one-to-one mapping between time-dependent densities and external potentials is established for a fixed initial state ψ_0.

$$\{V_{\mathrm{n}}(\underline{\mathbf{R}},t),V_{\mathrm{e}}(\mathbf{r},t)\}\xleftrightarrow{1-1}\{\Gamma(\underline{\mathbf{R}},t),\rho(\mathbf{r},t)\} \tag{16}$$

D. The time-dependent Kohn-Sham scheme for multicomponent system

The multicomponent Kohn-Sham (MCKS) system consists of noninteracting electrons and nuclei. The key assumption in the MCKS scheme is that the local effective potentials $\{\widehat{V}_{\mathrm{S,n}},\widehat{V}_{\mathrm{S,e}}\}$ exist such that the densities of the auxiliary system reproduce the exact densities of the fully interacting system. If this assumption holds true then the exact densities are given by

$$\begin{aligned}\Gamma(\underline{\mathbf{R}},t) &= |\chi(\underline{\mathbf{R}},t)|^2 \ , && (17)\\ \rho(\mathbf{r},t) &= \sum_{j=1}^{N_{\mathrm{e}}}|\varphi_j(\mathbf{r},t)|^2 \ , && (18)\end{aligned}$$

where χ and φ_j are the solutions of an N_{n}-particle nuclear and a single-particle electronic Schrödinger equation

$$\begin{aligned}i\frac{\partial}{\partial t}\chi(\underline{\mathbf{R}},t) &= \left(-\sum_\alpha\frac{\nabla_\alpha^2}{2M_\alpha}+V_{\mathrm{S,n}}[\Gamma,\rho](\underline{\mathbf{R}},t)\right)\chi(\underline{\mathbf{R}},t) \ , && (19)\\ i\frac{\partial}{\partial t}\varphi(\mathbf{r},t) &= \left(-\frac{\nabla^2}{2}+V_{\mathrm{S,e}}[\Gamma,\rho](\mathbf{r},t)\right)\varphi_j(\mathbf{r},t) \ . && (20)\end{aligned}$$

The effective potentials reproducing the exact densities are given by

$$\begin{aligned}V_{\mathrm{S,n}}[\Gamma,\rho](\underline{\mathbf{R}},t) &= V_{\mathrm{n}}(\underline{\mathbf{R}},t)+V_{\mathrm{Hxc,n}}[\Gamma,\rho](\underline{\mathbf{R}},t) \ , && (21)\\ V_{\mathrm{S,e}}[\Gamma,\rho](\mathbf{r},t) &= V_{\mathrm{e}}(\mathbf{r},t)+V_{\mathrm{Hxc}}[\Gamma,\rho](\mathbf{r},t) \ . && (22)\end{aligned}$$

For each of the two potentials, the remaining term with subscript “Hxc” denotes the sum of Hartree, exchange and correlation potentials. Equations (17)–(22) are the essence of the time-dependent MCKS scheme. The dynamics of an interacting many-particle system can be calculated by propagating a set of single-particle equations. In the presence of an external field the nuclei cannot be considered as static and the nuclear motion (vibration and rotation) has to be taken in to account. The TD-MCKS scheme allows for a non-perturbative treatment of external fields of arbitrary strength and the electronic and nuclear motion are treated on similar footing. However, the success of the proposed approach relies on the quality of approximation for the “Hxc” potentials.

III. CONSTRUCTION OF THE EXACT KOHN-SHAM POTENTIAL FOR A MODEL SYSTEM

A. The model system

We consider a one-dimensional (1D) H_2^+ molecular ion (where the motion of the particles is confined to one dimension) as a reference system. This model system is characterized by the Hamiltonian

$$\widehat{H}(x,R)=\widehat{T}_{\mathrm{n}}+\widehat{T}_{\mathrm{e}}+W_{\mathrm{en}}^{1D}(x,R)+W_{\mathrm{nn}}^{1D}(R) \tag{23}$$

with $\widehat{T}_{\mathrm{n}}=-\frac{1}{2\mu_{\mathrm{n}}}\frac{d^2}{dR^2}$ and $\widehat{T}_{\mathrm{e}}=-\frac{1}{2\mu_{\mathrm{e}}}\frac{d^2}{dx^2}$. Here μ_{n} and μ_{e} denote the reduced mass of nuclei and electron respectively. "x" denotes the electron coordinate and "R" denotes the internuclear distance. In our model the bare Coulomb potentials are replaced by soft-Coulomb potentials,

$$W_{\mathrm{en}}^{1D}(x,R)=-\frac{1}{\sqrt{(x-\frac{R}{2})^2+a_{\mathrm{e}}}}-\frac{1}{\sqrt{(x+\frac{R}{2})^2+a_{\mathrm{e}}}}\ , \tag{24}$$

$$W_{\mathrm{nn}}^{1D}(R)=\frac{1}{\sqrt{R^2+a_{\mathrm{n}}}}\ . \tag{25}$$

Here $a_{\mathrm{e}}=1$ and $a_{\mathrm{n}}=0.03$ are the soft-core parameters. The ground state is obtained by the split-operator (SPO) method and imaginary time propagation. This ground-state wave function $\psi(x,R)$ gives the exact densities $\Gamma(R)$ and $\rho(x)$ according to

$$\Gamma(R)=\int dx|\psi(x,R)|^2\ , \tag{26}$$

$$\rho(x)=\int dR|\psi(x,R)|^2\ . \tag{27}$$

The advantages of using the 1D model are the following: 1) No Coriolis term is present in the Hamiltonian (as there are no rotations in the 1D case). 2) Reduced computational effort. 3) Qualitative description of the dynamics in a real 3D system is possible.

B. Retrieval of the exact Kohn-Sham potentials

In [6] Lein and Kümmel presented an approach to obtain the exact time-dependent KS and exchange-correlation potentials for the strong-field dynamics of a correlated system. We start our discussion with the time-dependent Schrödinger equation,

$$i\frac{\partial\psi(x,R,t)}{\partial t}=\widehat{H}(t)\psi(x,R,t)\ . \tag{28}$$

In order to generate the exact KS potential two hurdles have to be overcome. First we have to generate the quasi-exact density of the system. Second, an algorithm to construct the KS potential is needed.

By time-propagation of the initial state, we get the nuclear/electronic density by integrating the absolute square of 2D wave function, $|\psi(x, R, t)|^2$, over the electronic/nuclear coordinates,

$$\Gamma(R, t) = \int |\psi(x, R, t)|^2 dx \ , \tag{29}$$

$$\rho(x, t) = \int |\psi(x, R, t)|^2 dR \ . \tag{30}$$

Similarly we evaluate the nuclear/electronic current from the following equations:

$$j_{\mathrm{n}}(R, t) = \frac{1}{\mu_{\mathrm{n}}} \mathrm{Re} \int \psi^*(x, R, t) \frac{\partial}{i\partial R} \psi(x, R, t) dx \ , \tag{31}$$

$$j_{\mathrm{e}}(x, t) = \frac{1}{\mu_{\mathrm{e}}} \mathrm{Re} \int \psi^*(x, R, t) \frac{\partial}{i\partial x} \psi(x, R, t) dR \ . \tag{32}$$

Equipped with density and current we can construct the KS orbitals as follows:

$$\chi(R, t) = \sqrt{\Gamma(R, t)} e^{i\alpha_{\mathrm{n}}(R,t)} \ , \tag{33}$$

$$\phi(x, t) = \sqrt{\rho(x, t)} e^{i\alpha_{\mathrm{e}}(x,t)} \ , \tag{34}$$

where α_{n} and α_{e} are the phases of the respective orbital. They can be calculated up to a time-dependent constant from

$$\frac{\partial \alpha_{\mathrm{n}}(R, t)}{\partial R} = \mu_{\mathrm{n}} \ \frac{j_{\mathrm{n}}(R, t)}{\Gamma(R, t)} \ , \tag{35}$$

$$\frac{\partial \alpha_{\mathrm{e}}(x, t)}{\partial x} = \mu_{\mathrm{e}} \ \frac{j_{\mathrm{e}}(x, t)}{\rho(x, t)} \ . \tag{36}$$

After obtaining the KS orbitals, the KS potential for nuclei as well as electrons can be obtained by inversion of the split-operator time propagator [6]:

$$V_{\mathrm{S,n}}(R, t) = -\frac{1}{2\delta t} \arcsin \left[\mathrm{Im} \left(\frac{e^{+i\widehat{T}_{\mathrm{n}}\delta t} \chi(R, t + \delta t)}{e^{-i\widehat{T}_{\mathrm{n}}\delta t} \chi(R, t - \delta t)} \right) \right] + C(t) \ , \tag{37}$$

$$V_{\mathrm{S,e}}(x, t) = -\frac{1}{2\delta t} \arcsin \left[\mathrm{Im} \left(\frac{e^{+i\widehat{T}_{\mathrm{e}}\delta t} \phi(x, t + \delta t)}{e^{-i\widehat{T}_{\mathrm{e}}\delta t} \phi(x, t - \delta t)} \right) \right] + c(t) \ . \tag{38}$$

The nuclear correlation potential $V_{\mathrm{c,n}}$ and electronic correlation potential $V_{\mathrm{c,e}}$ are defined by

$$V_{\mathrm{S,n}}(R, t) = W_{\mathrm{nn}}(R) + V_{\mathrm{H,n}}(R, t) + V_{\mathrm{c,n}}(R, t) \ , \tag{39}$$

$$V_{\mathrm{S,e}}(x,t) = V_{\mathrm{H,e}}(x,t) + V_{\mathrm{c,e}}(x,t) \ . \tag{40}$$

There are no exchange term and electron-electron Coulomb repulsion term present in the case of the H_2^+ molecular ion. The Hartree potentials in Equations (39) and (40) are given by

$$V_{\mathrm{H,n}}(R,t) = \int W_{\mathrm{en}}(x,R)\rho(x,t)dx \ , \tag{41}$$

$$V_{\mathrm{H,e}}(x,t) = \int W_{\mathrm{en}}(x,R)\Gamma(R,t)dR \ . \tag{42}$$

Therefore the correlation potentials can be easily calculated from Equations (39), (40) once the KS potentials are known.

We also perform Born-Oppenheimer (BO) calculations for the model system discussed here. Comparing the ground-state nuclear KS potential with the ground-state BO potential energy surface (BO-PES) of the model system, a good agreement is found, see figure 1. We also note in passing that in the region where density is close to zero, the inversion of nuclear KS potential leads to numerical instabilities. Therefore in such a region we cannot exactly evaluate the nuclear potential. This can be seen in figure 1 at large internuclear distances.

IV. RESULTS

A. Field-free dynamics

We first study the model system in absence of any external field. To generate an initial state, the nuclear ground-state wave function, $\chi_{\mathrm{n}}^{\mathrm{BO,gr}}(R)$ is calculated within the Born-Oppenheimer (BO) approximation. The product of the BO nuclear wave function with an electronic state is chosen as the initial state. We consider three different choices:

$$\psi_{\mathrm{initial,gr}}(x,R) = \chi_{\mathrm{n}}^{\mathrm{BO,gr}}(R) \cdot \Phi_{\mathrm{e}}^{\mathrm{BO,gr}}(x|R) \ , \tag{43}$$

$$\psi_{\mathrm{initial,ex}}(x,R) = \chi_{\mathrm{n}}^{\mathrm{BO,gr}}(R) \cdot \Phi_{\mathrm{e}}^{\mathrm{BO,ex}}(x|R) \ , \tag{44}$$

$$\psi_{\mathrm{initial,ss}}(x,R) = \chi_{\mathrm{n}}^{\mathrm{BO,gr}}(R) \cdot \Big(\alpha\ \Phi_{\mathrm{e}}^{\mathrm{BO,gr}}(x|R) + \beta\ \Phi_{\mathrm{e}}^{\mathrm{BO,ex}}(x|R)\Big) \ , \tag{45}$$

where $\Phi_{\mathrm{e}}^{\mathrm{BO,gr}}(x|R)$ and $\Phi_{\mathrm{e}}^{\mathrm{BO,ex}}(x|R)$ are the electronic ground-state and first excited-state respectively. Here $\alpha(= 0.9)$ and $\beta(= 0.4358)$ indicate the weights in the superposition $(\alpha^2 + \beta^2 = 1)$. The different initial states are illustrated in figure 2.

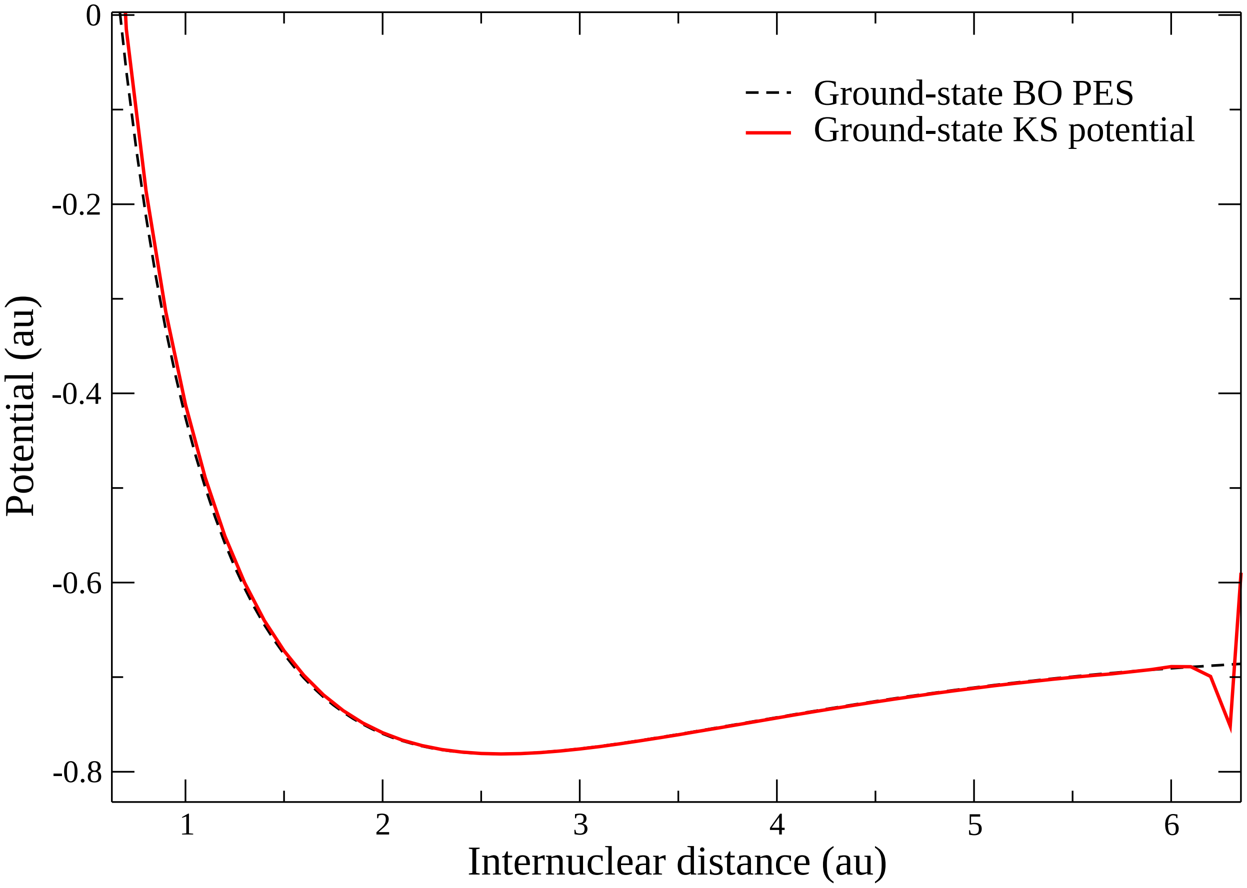

FIG. 1: A comparison between ground state BO-PES and KS potential

The wave function is then propagated in real time by SPO method and, at certain times, the time-dependent nuclear and electronic KS potentials are evaluated using the algorithm explained in the previous section.

The nuclear KS potential for the case of the electronic ground state (Equation (43)) is shown in figure 3. We also compare our results with the results obtained using alternative methods [7, 8]. Figure 3 shows the nuclear density (in column 1 and 3) and ground-state nuclear KS potential (in column 2 and 4) at various times. It is evident that the nuclear density remains stationary in time and the KS potential is similar to the ground-state BO-PES.

Similarly we perform the calculations for the BO first excited state (Equation (44)). In figure 4, we plot the nuclear density and corresponding nuclear KS potential at different times. Wave-packet motion on the PES is seen and the nuclear KS potential is similar to the excited state BO-PES.

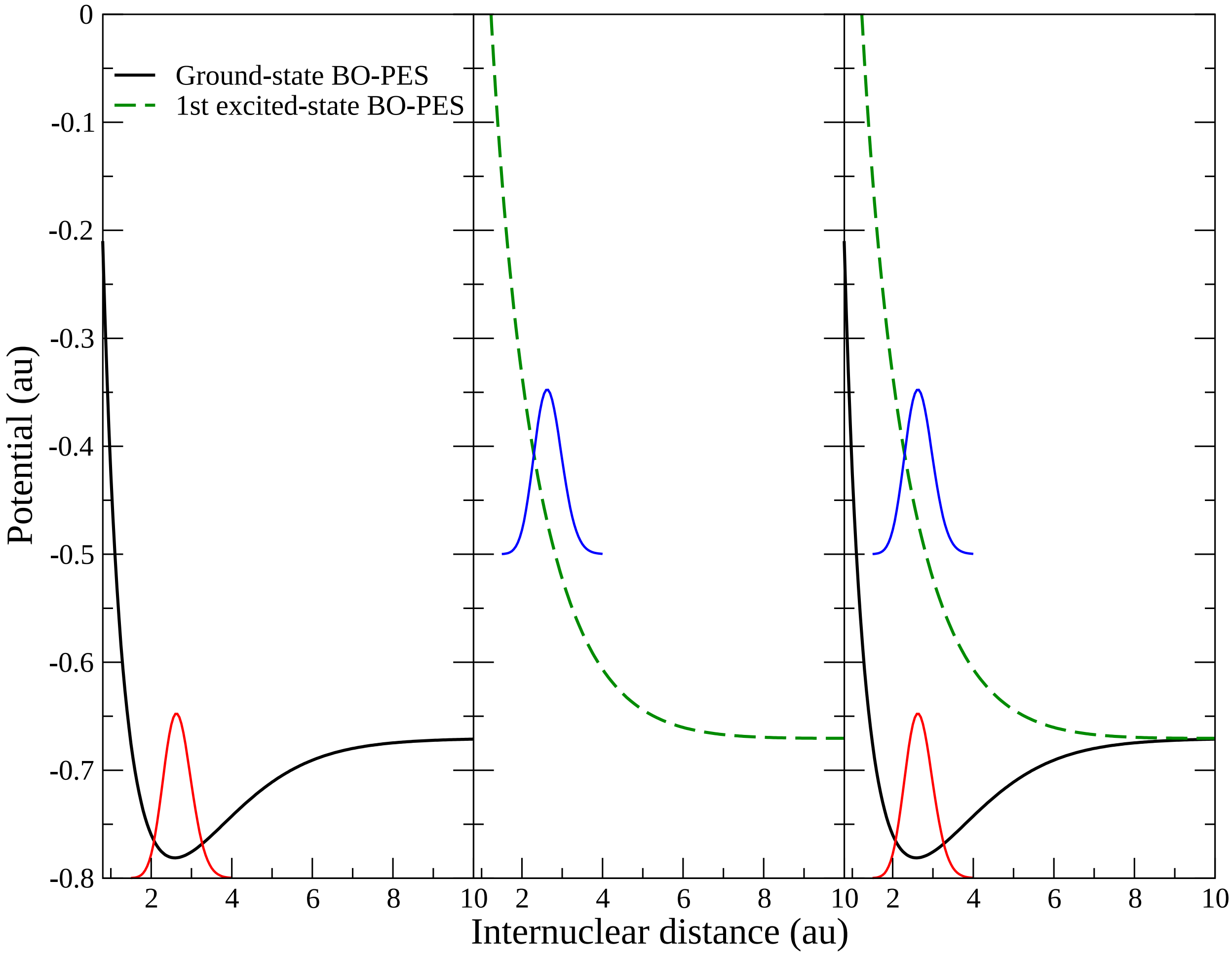

FIG. 2: Illustration of the three different initial states used for the time-dependent calculations, see text.

In the third case, the electronic state is a superposition of ground and excited states. This mimics the physical situation of photodissociation. The result is shown in figure 5. In figure 5 we also plot the ground-state and first excited-state BO-PES and the nuclear Hartree potential at various times for comparison. There is nice agreement of the KS potential with the ground-state BO-PES for small R and with the excited-state BO-PES for large R. There is a noticeable disagreement between the KS potential and the Hartree potential.

B. Dynamics in presence of an external field

In the presence of external field the Hamiltonian of Equation (23) is replaced by

$$\widehat{H}(t) = \widehat{T}_{\mathrm{n}} + \widehat{T}_{\mathrm{e}} + W_{\mathrm{en}}^{1D}(x,R) + W_{\mathrm{nn}}^{1D}(R) + V_{\mathrm{e}}(x,t) \ , \tag{46}$$

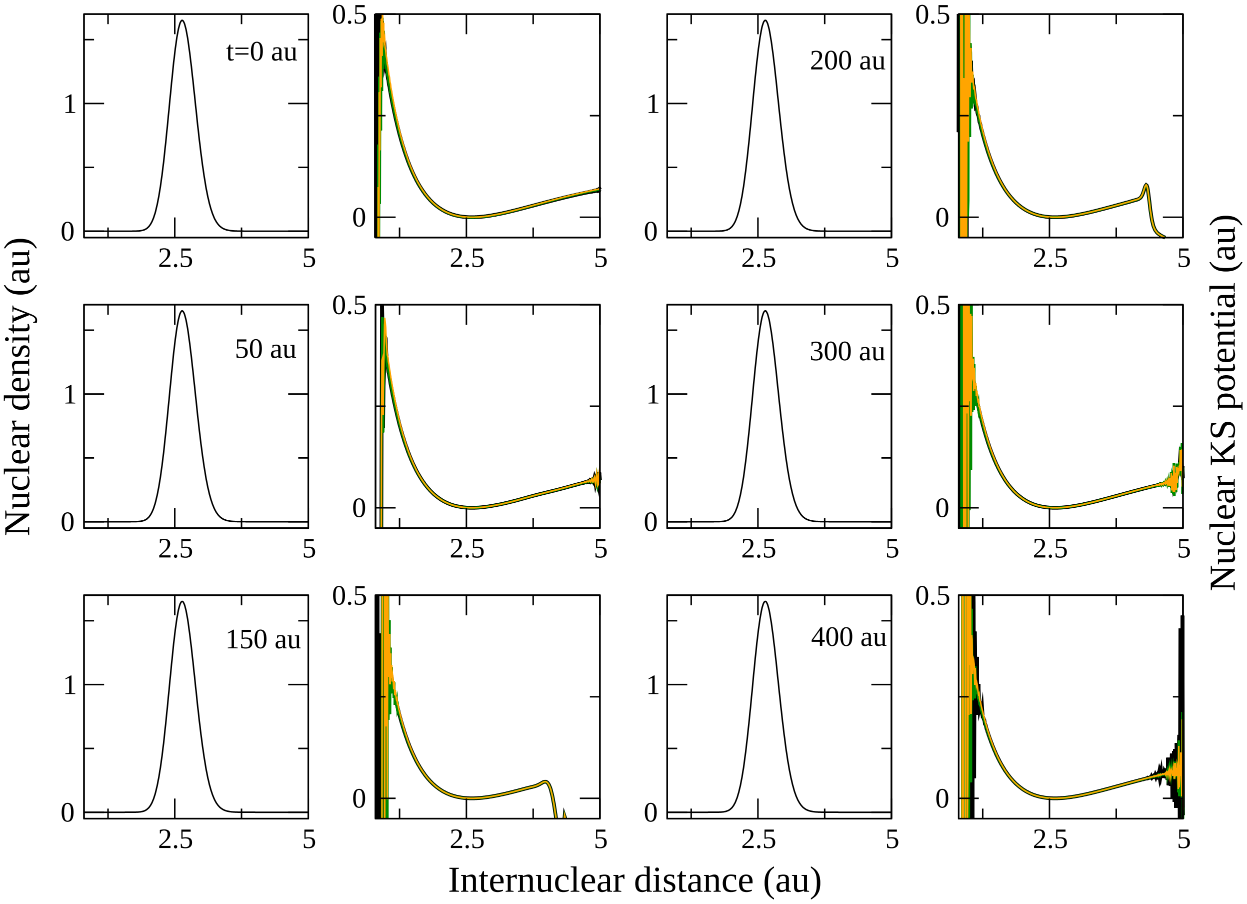

FIG. 3: Nuclear KS potential for a wave packet in the electronic ground state. In column 1 and 3 we plot the nuclear density at various times and the corresponding nuclear KS potential is shown in column 2 and 4. The black curve shows the results of the present calculation. The green curve [7] and orange curve [8] show the KS potentials obtained from alternative methods.

and Equation (40) is replaced by,

$$V_{\mathrm{S,e}}(x,t) = V_{\mathrm{e}}(x,t) + V_{\mathrm{H,e}}(x,t) + V_{\mathrm{c,e}}(x,t) \ . \tag{47}$$

We subject the model system to an electric field $E(t)$ that grows with time as $E(t) = E_0 \ \sin^2(t/\mathrm{c})$, with c = 458.5 a.u. To avoid numerical problems with strongly accelerated electrons, the interaction with the field is truncated at a distance of $x_{\mathrm{t}} = 50$ a.u. from the nucleus. The potential due to the external field can be written as

$$V_{\mathrm{e}}(x,t) = q_{\mathrm{e}} x E(t) \ \text{for} \ |x| < x_{\mathrm{t}} \ . \tag{48}$$

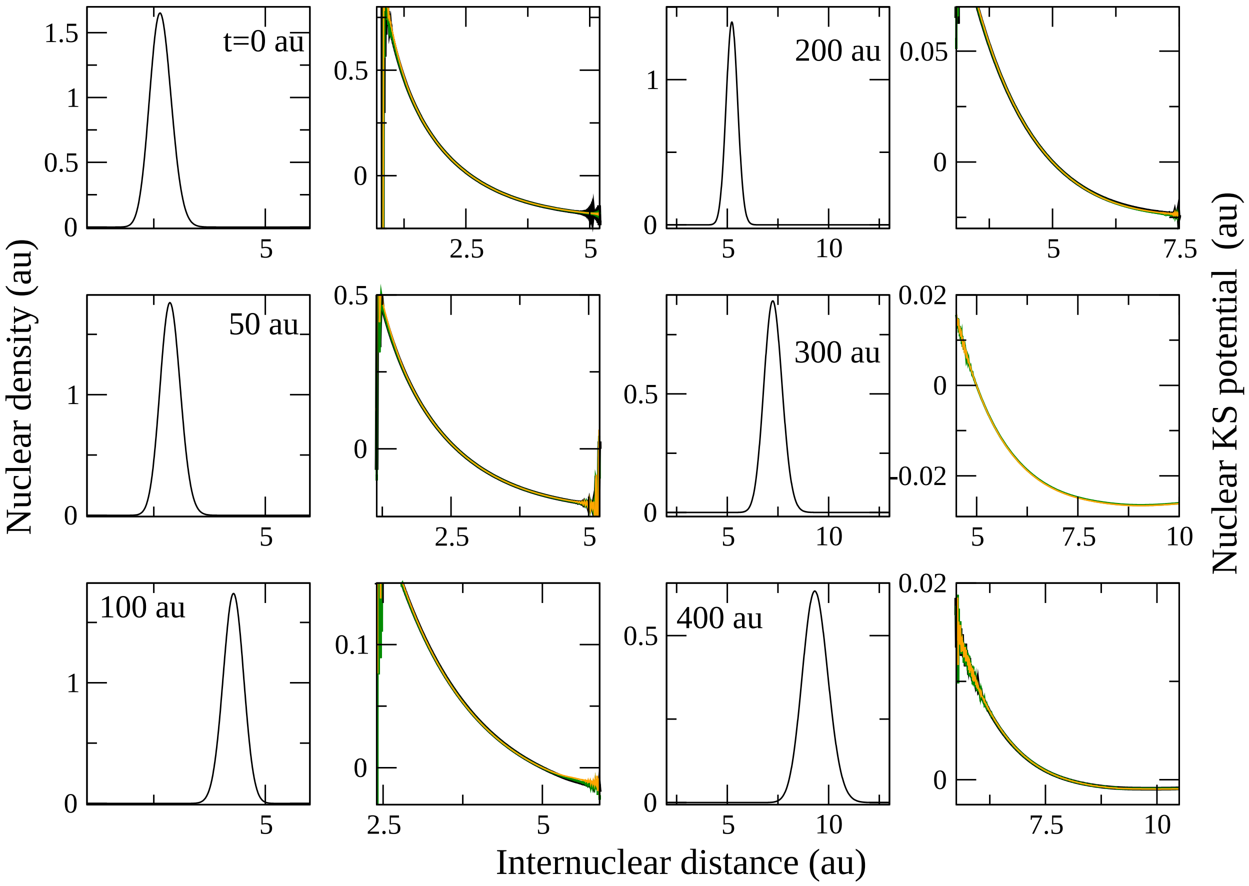

FIG. 4: Nuclear KS potential for a wave packet in the electronic excited state. In column 1 and 3 we plot the nuclear density at various times and the corresponding nuclear KS potential is shown in column 2 and 4. The black curve shows the results of the present calculation. The green curve [7] and orange curve [8] show the KS potentials obtained from alternative methods.

Here q_e denotes reduced charge given as

$$q_\mathrm{e} = \frac{2 + 2m_\mathrm{n}}{2m_\mathrm{n} + 1}. \tag{49}$$

The ground state is chosen as the initial state. In figures 6 and 7 we plot the nuclear KS potential for the model system subjected to fields of different strength. We see nice agreement between the KS potential and BO-PES for small R while the Hartree potential is not in agreement. After ionization, the bare protons repel each other due to Coulomb force. The Coulomb explosion is seen for large R in figures 6 and 7.

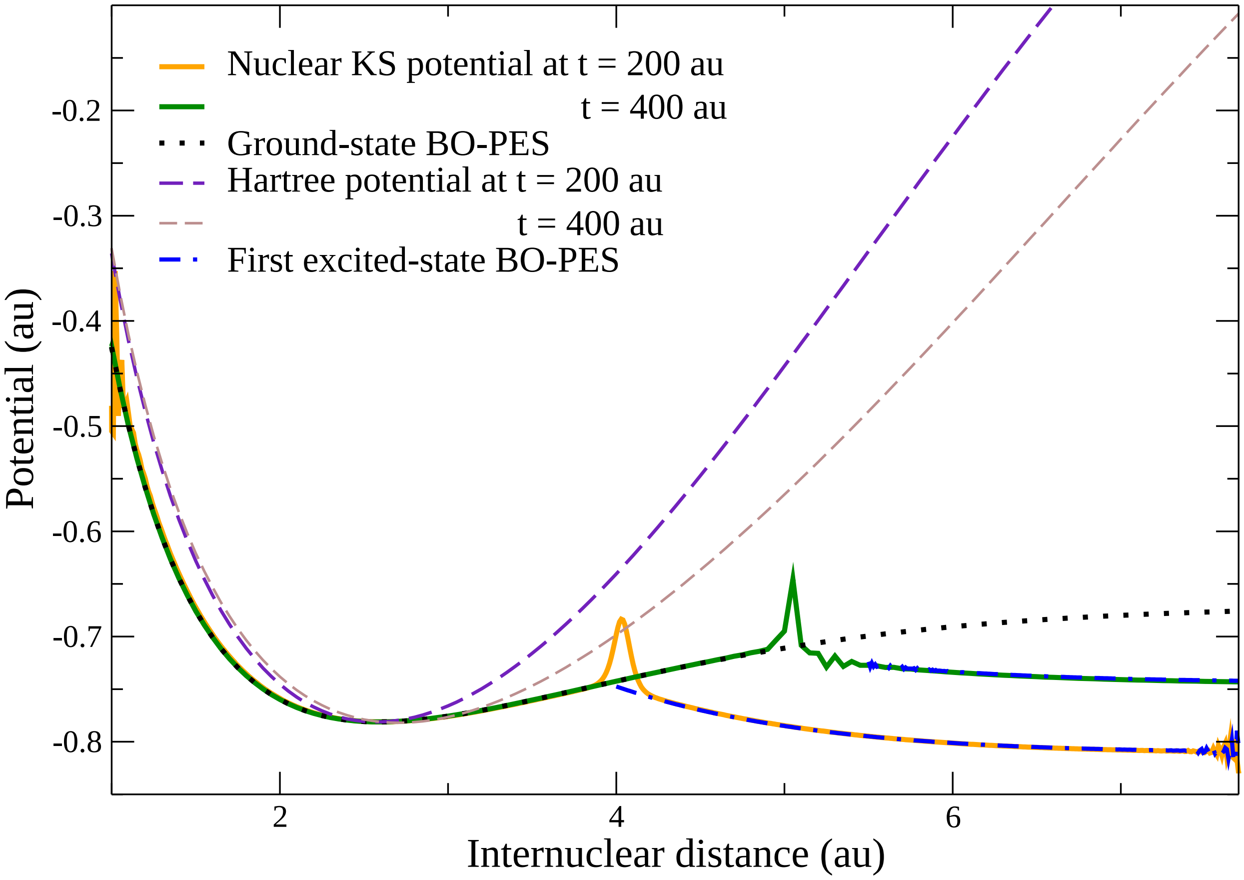

FIG. 5: Nuclear KS potential for wave packet in superposition state.

V. TIME-DEPENDENT MULTI-CONFIGURATION APPROACH

As an alternative approach to MCDFT, we propose in this section a version of the multi-configuration time-dependent Hartree (MCTDH) method [9] for electron and nuclei in H_2^+. This means that we specify an ansatz for the many-body wave function in terms of single-particle orbitals and apply the Dirac-Frenkel variational principle to obtain time-dependent orbitals.

In the simplest case, the wave function is represented as a Hartree product of single-particle functions.

$$\psi(x,R,t) = a(t)\ \chi(R,t)\ \phi(x,t)\ , \tag{50}$$

resulting in a set of coupled single-particle equations of motion for the functions χ and ϕ. This approach reduces the computational effort significantly, but at the cost that the correlation between the degrees of freedom is lost.

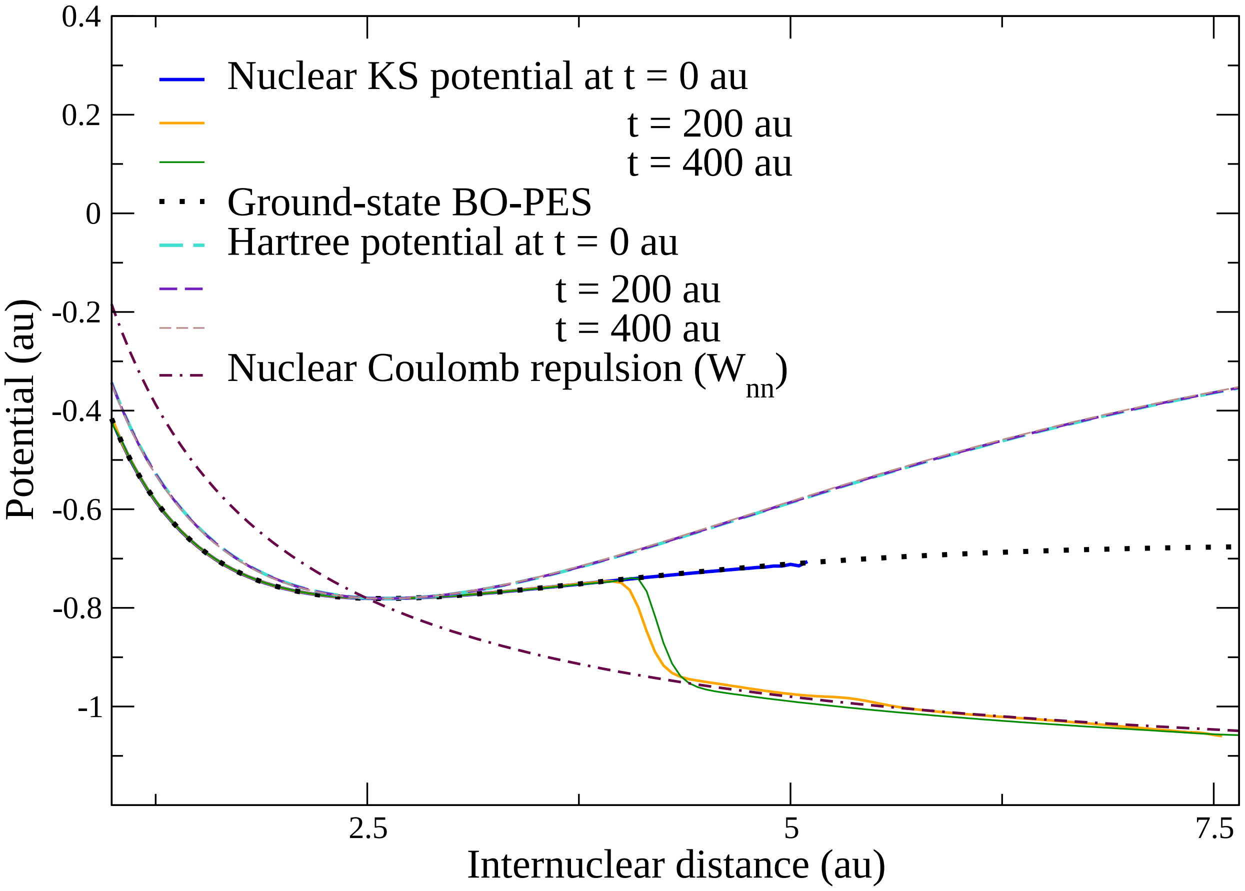

FIG. 6: Nuclear KS potential in the presence of a slowly switched on electric field (E=0.0100 a.u. at t=400 a.u.).

We find that the Hartree mean-field approach fails to reproduce the nuclear potential [10], indicating that the Hartree approximation needs to be improved. Figures 5, 6 and 7 support this statement. We therefore consider the MCTDH method using the ansatz

$$\psi(x, R, t) = \sum_{i=1}^{n} a_i(t)\ \chi_i(R, t)\ \phi_i(x, t)\ . \tag{51}$$

Preliminary results show that the ground-state energy is close to the exact value obtained from the exact calculations and is certainly improved compared to the Hartree ansatz.

VI. CONCLUSION AND OUTLOOK

We have discussed two approaches to go beyond the Hartree approximation for the dynamics of interacting electrons and nuclei. In the framework of MCDFT, we have calculated

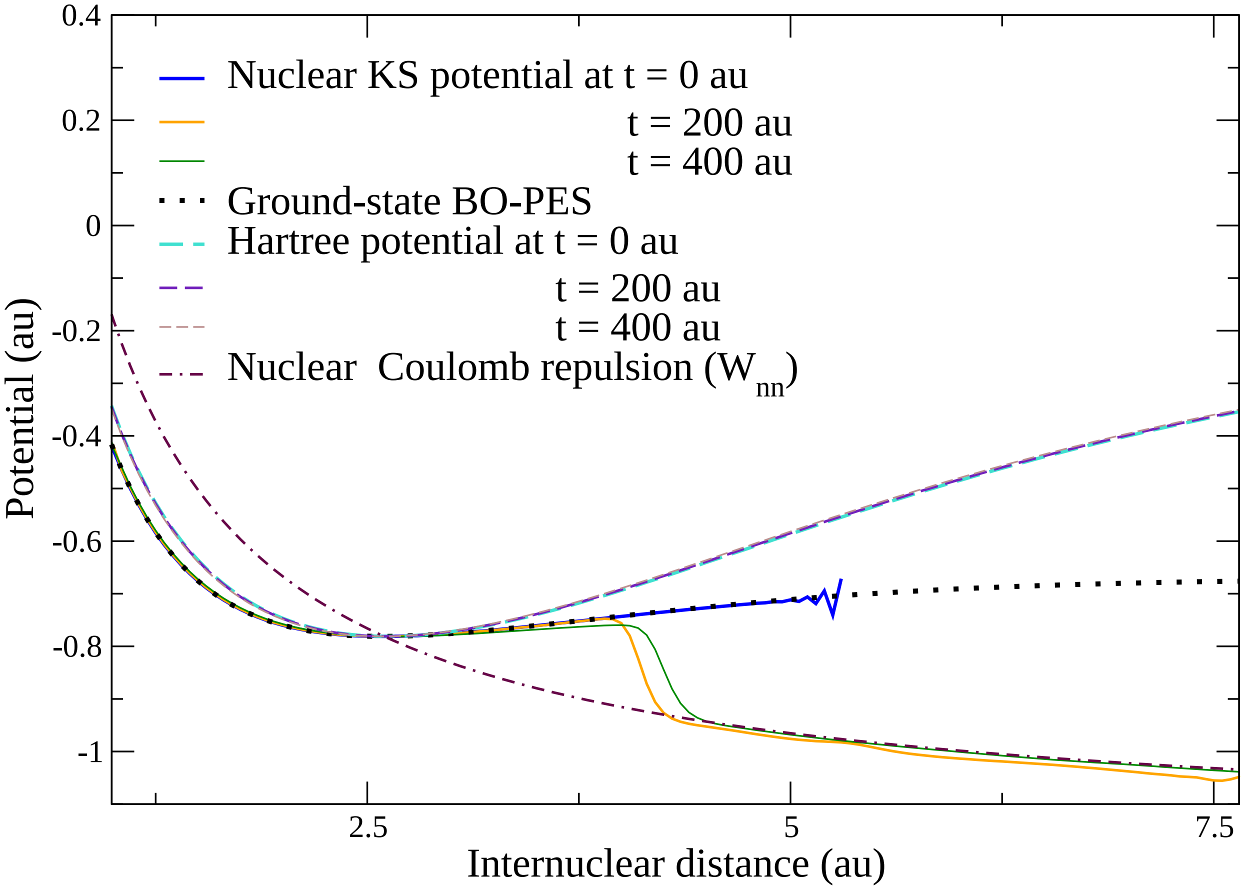

FIG. 7: Nuclear KS potential in the presence of a slowly switched on electric field (E=0.0316 a.u. at t=400 a.u.).

the exact time-dependent KS potentials and hope that these will be helpful in the construction of practical functionals.

The MCTDH formalism is well documented in literature [9], but so far it has not been applied to electrons and nuclei in external fields. Although computationally more demanding than the time-dependent MCDFT approach, it allows to systematically improve the accuracy towards the exact result.

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