

Towards time-dependent density-functional theory for molecules in strong laser pulses

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To describe the dynamical interplay of electronic and nuclear degrees of freedom in molecules exposed to strong laser pulses, we present two different variational approaches based on the stationary-action principle: A mean-field treatment of the electron-nuclear interaction and an explicitly correlated ansatz. The two methods are tested on a one-dimensional model of H_2^+ which can be solved exactly. The correlated approach significantly improves upon the mean-field treatment, especially in the case of laser fields strong enough to cause substantial dissociation.

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The past decade has witnessed rapid progress in laser technology. Nowadays, tabletop systems routinely provide femtosecond laser pulses with intensities in the terawatt regime. The field strengths at such intensities are comparable to or even larger than, typical atomic or molecular binding forces [1]. Therefore, an adequate description of strong-field multiphoton processes requires a non-perturbative scheme which treats the external laser field and the internal Coulomb forces of the atom or molecule on equal footing. While considerable progress has been made in understanding the behavior of atoms in high-intensity laser pulses, the situation for molecules is far less advanced since the additional nuclear degrees of freedom tremendously increase the complexity of the problem. The traditional methods like expanding the total molecular wavefunction in terms of few Born-Oppenheimer (BO) states or restricting oneself to a classical description of the nuclear degrees of freedom [2,3] cannot satisfactorily explain the complex interplay between the electronic and the nuclear motion. In fact, the direct numerical solution of the full time-dependent (TD) Schrödinger equation (SE) for the H_2^+ molecular ion [4] shows that a proper treatment of all fundamental processes, i.e., electronic and vibrational excitation, ionization, and dissociation, is mandatory in the high-intensity regime. However, even for this smallest possible molecule, the full-scale numerical solution of the electron-nuclear TDSE is barely feasible. Clearly, the strong-field dynamics of larger molecules requires an approximate treatment. To this end, we employ the stationary-action principle

$$\delta\mathcal{A}[\Psi] = \delta \int_{t_0}^{t_1} dt \langle \Psi(t) | i\partial_t - \hat{H}(t) | \Psi(t) \rangle = 0 \quad (1)$$

which, for any approximate form of the wavefunction Ψ , determines the corresponding equations of motion and thus the dynamical behavior of the system. In this Letter, we will present two different approximations for the total wavefunction Ψ : The first one is based on a mean-field-type treatment of the electron-nuclear coupling which neglects correlation effects between the electronic and the nuclear motion. The second approach

employs an explicitly correlated ansatz for the electron-nuclear part of the wavefunction. The crucial point of both approaches is that they provide a description in terms of single-particle orbitals. Only single-particle equations, by their very nature, can be solved with moderate numerical effort and thus bring within reach the TD treatment of larger systems.

For simplicity, we restrict ourselves to the discussion of diatomic molecules consisting of N_e electrons and two nuclei of masses M_1 and M_2 and charges Z_1 and Z_2 . Since we shall be interested in radiation sources in a regime where the dipole approximation holds true, the center-of-mass (CM) motion of the total system can be separated off. The molecule is then described by the vector of the internuclear distance \mathbf{R} and electronic coordinates $\underline{\mathbf{r}} \equiv \{\mathbf{r}_j\}$ referring to a molecular body-fixed frame whose z -axis \mathbf{e}_z is parallel to \mathbf{R} . In terms of these coordinates, the Hamiltonian in Eq. (1) reads (atomic units)

$$H(\underline{\mathbf{r}}, \mathbf{R}, t) = T(\underline{\mathbf{r}}, \mathbf{R}) + W(\underline{\mathbf{r}}, \mathbf{R}) + V_L(\underline{\mathbf{r}}, \mathbf{R}, t) \quad (2)$$

where $T = -(1/2\mu_n)\nabla_{\mathbf{R}}^2 - (1/2\mu_e)\sum_{j=1}^{N_e}\nabla_j^2$ with $\mu_n = (M_1M_2)/(M_1+M_2)$ and $\mu_e = (M_1+M_2)/(M_1+M_2+1)$ denotes the kinetic-energy operator, and $W = W_{ee} + W_{en} + W_{nn}$ contains the interactions between all particles. Mass-polarization and Coriolis terms are neglected. Furthermore, employing the length gauge, the laser potential in Eq. (2) is given by $V_L(t) = (-q_n\mathbf{R} + q_e\sum_j\mathcal{R}(\mathbf{R})\mathbf{r}_j)\mathbf{E}(t)$, where $\mathbf{E}(t)$ denotes the electric field amplitude, $q_n = (Z_1M_2 - Z_2M_1)/(M_1+M_2)$ and $q_e = (Z_1+Z_2+M_1+M_2)/(M_1+M_2+N_e)$. $\mathcal{R}(\mathbf{R})$ represents the 3×3 rotational matrix which rotates the internuclear axis \mathbf{R} (i.e., the z -axis of the body-fixed frame) into the z -axis of the CM-fixed coordinate system.

In our first approach, the total electron-nuclear many-body wavefunction is approximated by

$$\Psi(\mathbf{R}, \underline{\mathbf{r}}, t) \approx \chi(\mathbf{R}, t)\psi(\underline{\mathbf{r}}, t), \quad (3)$$

where $\chi(\mathbf{R}, t)$ is a TD nuclear wavefunction and $\psi(\underline{\mathbf{r}}, t)$ represents a TD electronic many-particle state. The stationary-action principle (1) with Hamiltonian (2) then

leads to a TDSE for the nuclear wavefunction

$$i\partial_t\chi(\mathbf{R},t) = \left(-\frac{\nabla_{\mathbf{R}}^2}{2\mu_n} + V_{S,n}(\mathbf{R},t)\right)\chi(\mathbf{R},t) \quad (4)$$

and to a many-body TDSE for $\psi(\underline{\mathbf{r}},t)$. Applying TD density-functional theory (TDDFT) [5–7] to the latter leads to a set of TD Kohn-Sham equations:

$$i\partial_t\varphi_j(\mathbf{r},t) = \left(-\frac{\nabla_{\mathbf{r}}^2}{2\mu_e} + v_{S,e}(\mathbf{r},t)\right)\varphi_j(\mathbf{r},t), \quad (5)$$

where $\{\varphi_j(\mathbf{r},t)\}$ are electronic Kohn-Sham orbitals. The local effective potentials $V_{S,n}$ and $v_{S,e}$ are given by

$$V_{S,n}(\mathbf{R},t) = V_{L,n}(\mathbf{R},t) + \frac{Z_1 Z_2}{R} + V_{H,n}^{en}(\mathbf{R},t) \quad (6)$$

$$v_{S,e}(\mathbf{r},t) = v_{L,e}(\mathbf{r},t) + v_{\text{Hxc}}^e(\mathbf{r},t) + v_{H,e}^{en}(\mathbf{r},t). \quad (7)$$

The last terms on the r.h.s. of Eqs. (6) and (7) denote the time-dependent Hartree (mean-field) potentials arising from the electron-nuclear interaction. By virtue of the ansatz (3), they are given by the classical electrostatic potentials caused by the respective charge distributions:

$$V_{H,n}^{en}(\mathbf{R},t) := \int d\mathbf{r} W_{en}(\mathbf{r},\mathbf{R})\rho(\mathbf{r},t) \quad (8)$$

$$v_{H,e}^{en}(\mathbf{r},t) := \int d\mathbf{R} W_{en}(\mathbf{r},\mathbf{R})\Gamma(\mathbf{R},t), \quad (9)$$

where $\Gamma(\mathbf{R},t) = |\chi(\mathbf{R},t)|^2$ and $\rho(\mathbf{r},t) = \sum_{j=1}^{N_e} |\varphi_j(\mathbf{r},t)|^2$. The electron-nuclear interaction is given by $W_{en}(\mathbf{r},\mathbf{R}) = Z_1 |\mathbf{r} - \frac{M_2}{M_1+M_2} R\mathbf{e}_z|^{-1} + Z_2 |\mathbf{r} + \frac{M_1}{M_1+M_2} R\mathbf{e}_z|^{-1}$. The second term on the r.h.s. of Eq. (7) is the Hartree-exchange-correlation (Hxc) potential arising from the TDDFT treatment of the electronic degrees of freedom. Finally, the first terms on the r.h.s. of Eqs. (6) and (7) represent the laser potentials given by $V_{L,n}(\mathbf{R},t) = -q_n \mathbf{R}\mathbf{E}(t)$ and $v_{L,e}(\mathbf{r},t) = q_e \int d\mathbf{R} \Gamma(\mathbf{R},t) (\mathcal{R}(\mathbf{R})\mathbf{r}) \mathbf{E}(t)$.

In order to assess the accuracy of the scheme presented above, we apply it to a simplified model of the H_2^+ molecule which can be solved exactly. In this model, the dimensionality of the problem is reduced by confining the dynamics of all particles to one spatial dimension, i.e., the particles are allowed to move only in the direction of the laser polarization axis. Extensive studies have demonstrated that this model qualitatively reproduces all typical non-linear phenomena observed in strong-field experiments [8]. We emphasize that our primary interest is *not* the analysis of this model system. Instead, we aim at an ab-initio description of larger molecules exposed to strong laser fields. However, in order to assess the quality of the approximations employed, it is essential to have a numerically exact reference solution, to which the approximate results can be compared. The 1D model H_2^+ molecule naturally lends itself for that purpose.

The exact reference solution of the TDSE for the model H_2^+ molecule as well as the corresponding solution of the

approximate equations of motion (4), (5) are obtained numerically by employing the split-operator technique [9]. The initial wavefunctions are chosen as the respective molecular ground states. As an example, we investigate the dynamics of the model H_2^+ molecule in a $\lambda = 770$ nm, 77 fs laser field, where the laser is linearly ramped from zero to its maximum value within 12.5 optical cycles and subsequently kept constant for another 17.5 optical cycles. Fig. 1 shows the time evolution of the expectation value of the internuclear separation $\langle R \rangle(t)$ for a peak laser intensity of $I_0 = 7.5 \times 10^{13}$ W/cm² as obtained from the exact solution (solid line) and from the approximate scheme (dashed line). As seen in this figure, the laser field causes the molecule to stretch in the beginning of the propagation. However, the field is not strong enough to substantially dissociate the system. Instead, the molecule starts to vibrate, which is reflected in the oscillatory structure of the mean internuclear distance $\langle R \rangle(t)$. Compared to the exact results, we find that, for the laser parameters considered here, the approximate scheme reproduces the main features of the dynamics: $\langle R \rangle(t)$ initially increases and subsequently oscillates, although on a quantitative level, the amplitude of the oscillations of $\langle R \rangle(t)$ is underestimated while its frequency is overestimated.

In order to analyze the origin of these deviations, we investigate the potential $V_{H,n}^{en}(\mathbf{R},t)$ of the nuclear single-particle equation (4). This quantity is inherently time-dependent, but still it is instructive to consider the static nuclear potential resulting from the stationary ground-state solution of Eqs. (4) and (5) with the laser field switched off. In Fig. 2, this static nuclear ground-state potential is compared with the lowest-energy BO surface, which provides a very good reference for the ground state of the H_2^+ model molecule. The mean-field nuclear potential is in good agreement with the BO curve only in the neighborhood of the equilibrium internuclear separation. For larger values of R , the approximate nuclear potential severely deviates from the reference curve. From this perspective, the deviations of the strong-field behavior are easily understood: Compared to the exact dynamics, the approximate scheme requires much more energy to stretch the molecule. Consequently, if the same laser parameters are used in the exact and the approximate calculation, the latter will significantly underestimate the nuclear motion, leading to the deviations found in $\langle R \rangle(t)$. Likewise, for laser parameters leading to substantial dissociation, the mean-field approach is found to underestimate the dissociation probability significantly as shown in Fig. 3. Hence, we conclude that a mean-field-type approximation for the electron-nuclear interaction cannot, provide a satisfactory picture of the strong-field dynamics of molecules.

In order to improve upon the mean-field approach, electron-nuclear correlation needs to be incorporated in

the approximate form of the total wavefunction Ψ . We propose the explicitly correlated expression

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \chi(\mathbf{R}, t) \varphi_{\mathbf{R}}(\mathbf{r}, t), \quad (10)$$

$$\varphi_{\mathbf{R}}(\mathbf{r}, t) := \phi_1(\mathbf{r} - \frac{R}{2}\mathbf{e}_z, t) + \phi_2(\mathbf{r} + \frac{R}{2}\mathbf{e}_z, t)$$

where, $\chi(\mathbf{R}, t)$ again denotes the nuclear wavefunction. However, in contrast to the mean-field approach (3), the electronic degrees of freedom are not described by molecular orbitals, but by explicitly TD atomic orbitals $\phi_{1,2}(\mathbf{r}, t)$ which are attached to one of the nuclei. In other words, the correlation between the electron and the nuclei is introduced by referring the electron, in the spirit of a Heitler-London ansatz, to one or the other nucleus. The variationally best wavefunction of the form (10) is obtained by requiring the action to be stationary with respect to variations of all orbitals. This leads to [10] the equations of motion:

$$i\partial_t\chi(\mathbf{R}, t) = \left(\hat{h}_n(\mathbf{R}, t) - \Lambda(t)\right)\chi(\mathbf{R}, t), \quad (11)$$

$$i\partial_t\phi_{1,2}(\mathbf{r}, t) = \hat{h}_{e1,2}\phi_{1,2}(\mathbf{r}, t) + \mathcal{Q}_{1,2}(\mathbf{r}, t) \quad (12)$$

with the effective nuclear Hamiltonian

$$\hat{h}_n(\mathbf{R}, t) := -\frac{1}{2\mu_n}\nabla_{\mathbf{R}}^2 - \frac{1}{\mu_n}\langle\nabla_{\mathbf{R}}\rangle_e(\mathbf{R}, t)\nabla_{\mathbf{R}} + \langle\hat{H} - i\partial_t\rangle_e(\mathbf{R}, t). \quad (13)$$

and the effective electronic Hamiltonian

$$\hat{h}_{e1,2} := -\frac{1}{2\tilde{\mu}_e}\nabla_{\mathbf{r}}^2 \pm \frac{1}{2\mu_n}\langle\nabla_{\mathbf{R}}\rangle_n\nabla_{\mathbf{r}} + \langle\hat{H}(\mathbf{r} \pm R/2\mathbf{e}_z, \mathbf{R}) - \hat{T}_e - i\partial_t\rangle_n \quad (14)$$

where $\tilde{\mu}_e = 4\mu_n\mu_e/(4\mu_n + \mu_e)$, and $\mathcal{Q}_{1,2}(\mathbf{r}, t)$ denotes the inhomogeneity term : $\mathcal{Q}_{1,2}(\mathbf{r}, t) := \langle(\hat{H}(\mathbf{r} \pm R/2\mathbf{e}_z, \mathbf{R}) - i\partial_t)\phi_{2/1}(\mathbf{r} \pm R\mathbf{e}_z, t)\rangle_n$. For ease of notation, the following abbreviations have been introduced: $\langle\hat{\mathcal{O}}\rangle_e \equiv \langle\hat{\mathcal{O}}\rangle_e(\mathbf{R}, t) := \langle\varphi_{\mathbf{R}}|\hat{\mathcal{O}}|\varphi_{\mathbf{R}}\rangle_e/\langle\varphi_{\mathbf{R}}|\varphi_{\mathbf{R}}\rangle_e$ and $\langle\hat{\mathcal{O}}\rangle_n \equiv \langle\hat{\mathcal{O}}\rangle_n(\mathbf{r}, t) := \langle\chi|\hat{\mathcal{O}}|\chi\rangle_n/\langle\chi|\chi\rangle_n$, where the subscripts “e” or “n” indicate the integration over the electronic or nuclear coordinate, respectively. Eqs. (11) and (12) form the heart of the new time-dependent variational scheme which, like the mean-field approach treats the strong external fields $V_{L,n}(t)$ and $v_{L,e}(t)$ and the intramolecular forces on the same footing in a non-perturbative way. Furthermore, the method properly accounts for the quantum nature of both the electronic and the nuclear degrees of freedom. In this respect, the proposed variational approach goes beyond the common mixed classical-quantum mechanical methods where the nuclear dynamics is treated classically. On the other hand, in contrast to methods employing the wavepacket propagation on few BO potential-energy surfaces, the influence of the strong laser field on the time evolution of the electrons is consistently incorporated as well.

Still, although an explicitly correlated ansatz for the total wavefunction is used, it is important to realize that the dynamics is completely described in terms of single-particle orbitals. Consequently, the computational effort to solve Eqs. (11, 12) stays manageable. Considering these equations of motion individually, we observe the following features: The electronic equation (12) differs significantly from the corresponding mean-field equation (5). Whereas the latter describes the time evolution of molecular single-particle orbitals, the former propagates TD single-particle atomic orbitals. Consequently, additional inhomogeneity terms appear in Eq. (12) which act as source or sink terms and are responsible for the (laser-induced) transfer of electronic charge between the two nuclei. Considering the effective electronic potentials, the contribution arising from the electron-nuclear interaction is given by $\langle W_{en}(\mathbf{r} \pm R/2\mathbf{e}_z, \mathbf{R})\rangle_n(\mathbf{r}, t) = -1/r - (1/\langle\chi|\chi\rangle_n)\int d\mathbf{R} (|\chi(\mathbf{R}, t)|^2/|\mathbf{r} \pm R\mathbf{e}_z|)$. Accordingly, the electron feels the bare Coulomb force of its reference nucleus and a Hartree-type potential from the second nucleus. In particular, due to the dependence of $\langle W_{en}\rangle$ on the time-dependent orbital $\chi(\mathbf{R}, t)$, the formalism presented above naturally includes the quasistatic picture of molecular strong-field dynamics [11], which, e.g., successfully describes enhanced ionization leading to dissociative Coulomb explosion [12]. Turning to the nuclear equation of motion (11), we find that it is formally similar to Eq. (4). In particular, it again employs inherently TD effective potentials such that the nuclear dynamics is not restricted to a fixed potential-energy surface, but non-adiabatic processes can be described even by employing only one TD nuclear potential. The TD effective nuclear potential is explicitly given by the expectation value of $\hat{H} - i\partial_t$ with respect to $\varphi_{\mathbf{R}}(\mathbf{r}, t)$, as seen from the last term of Eq. (13). Due to the Heitler-London-type form of $\varphi_{\mathbf{R}}$ which is correct in the asymptotic ($R \rightarrow \infty$) limit the description of the effective nuclear potential and thus of the nuclear dynamics should be improved as compared to the TD mean-field scheme.

We employ again the same model H_2^+ to calculate the effective nuclear potential $V_n(R) = \langle\hat{H}_e\rangle_e(R)$ obtained from a self-consistent ground-state solution of the variational equations (11) and (12) (with the laser field switched off). Evidently, the resulting nuclear potential, as shown in Fig. 2, improves significantly upon the mean-field curve and only shows small deviations from the reference potential for $R \gtrsim 5$ a.u. Since the deviations of the nuclear mean-field potential were identified as the main source of error in the TD Hartree approach, the correlated variational scheme promises a more adequate treatment of the strong-field dynamics. This is confirmed by the results obtained for the dynamics of the model. The time evolution of the mean internuclear

distance $\langle R \rangle(t)$, for the same laser parameters, is shown in Figs. 1,3 and the improvement is obvious. In Fig. 1 the agreement is excellent and even in the case of the strong field in Fig. 3, leading to considerable photodissociation, the qualitative picture is correct.

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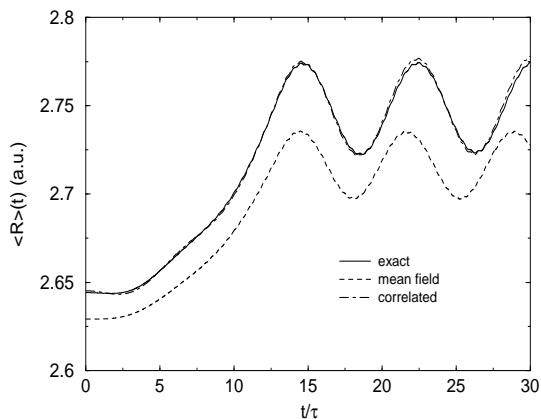


FIG. 1. Time evolution (in units of the optical cycle τ) of the mean internuclear distance $\langle R \rangle(t)$ obtained for the model H_2^+ molecule, in a $\lambda = 770$ nm, $I_0 = 7.5 \times 10^{13}$ W/cm² laser field from the various methods described in the text.

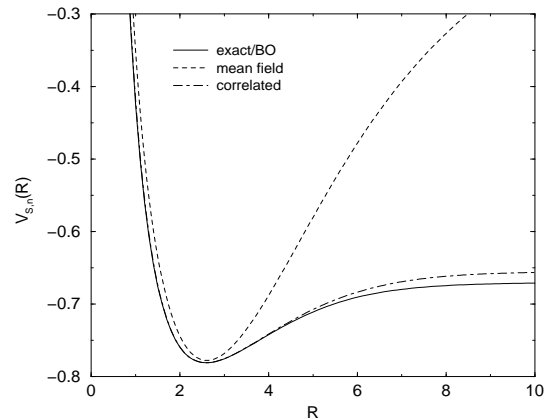


FIG. 2. Effective nuclear potential $V_{S,n}(R)$ obtained for the model H_2^+ from the methods described. Atomic units.

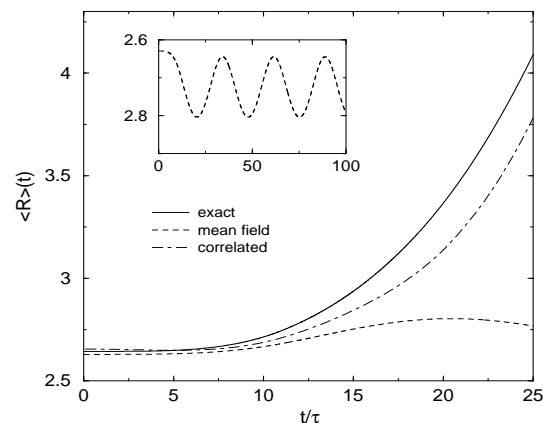


FIG. 3. Time evolution of $\langle R \rangle(t)$ for the model H_2^+ , in a $\lambda = 228$ nm, $I_0 = 2.5 \times 10^{13}$ W/cm² laser. In the insert, the mean field solution for a period of 100 τ .