

Ab-initio variational wave functions for the time-dependent many-electron Schrödinger equation

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Understanding the real-time evolution of many-electron quantum systems is essential for studying dynamical properties in condensed matter, quantum chemistry, and complex materials, yet it poses a significant theoretical and computational challenge. Our work introduces a variational approach for fermionic time-dependent wave functions, surpassing mean-field approximations by accurately capturing many-body correlations. We employ time-dependent Jastrow factors and backflow transformations, enhanced through neural networks parameterizations. To compute the optimal time-dependent parameters, we employ the time-dependent variational Monte Carlo technique and introduce a new method based on Taylor-root expansions of the propagator, enhancing the accuracy of our simulations. The approach is demonstrated in three distinct systems. In all cases, we show clear signatures of many-body correlations in the dynamics. The results showcase the ability of our variational approach to accurately describe the time evolution, providing insight into quantum dynamical effects in interacting electronic systems, beyond the capabilities of mean-field.

Grasping the consequences of interactions in quantum many-electron systems is necessary for a wide range of applications, including the prediction of the electronic structure in quantum chemistry^{1,2}, properties of crystalline solids³, insulating or (super)conducting behavior of complex materials^{4,5}. In addition to experiments, our main source of available information originates from numerical simulations of these systems. A significant amount of effort has been devoted to developing scalable and accurate techniques to obtain the (equilibrium) ground and excited states of interacting many-body systems, by solving the time-independent Schrödinger equation (TISE)

$$\hat{H}|\Psi\rangle = E|\Psi\rangle. \quad (1)$$

Real-time electron dynamics encompasses the explicit consideration of the time evolution of a quantum electronic system out of equilibrium. The problem boils down to capturing the time-dependent

quantum state $|\Psi(t)\rangle$, by solving the time-dependent Schrödinger equation (TDSE),

$$i\frac{d|\Psi(t)\rangle}{dt} = \hat{H}(t)|\Psi(t)\rangle, \quad (2)$$

subject to a time-dependent Hamiltonian $\hat{H}(t)$. Exploration of the time-dependent characteristics of quantum systems extends across various disciplines, encompassing phenomena such as correlated electrons in metal clusters, quantum dots, and ultracold Fermi gases^{6–10}. Within these systems, there exists a rich interplay of static and dynamic behaviors, often governed by collective modes arising from strong coupling effects^{10–12}.

Real-time quantum dynamics has received comparatively less attention than solving the TISE, primarily because of its significantly increased difficulty level. The latter is a consequence of the fact that a

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quantum system tends to traverse a larger portion of the configuration (Hilbert) space than the subspace containing ground states. Therefore, heuristics developed for static problems are not directly applicable. More specifically, it is no longer feasible to restrict the calculations to the low-entanglement corner of the Hilbert space^{13–15}. Obtaining the time-evolving quantum state of a time-dependent Hamiltonian, as described by the TDSE in Eq. (2), is traditionally achieved through a series of approximations. A commonly adopted approach to solving the TDSE approximately is to ignore electron-electron correlations, as is done in mean-field approximations. The first work in this direction comes from Dirac and Frenkel, from whom the time-dependent Hartree–Fock (TDHF) equations were obtained for electronic systems^{16,17}. Later, MacLachlan improved on this method¹⁸. Furthermore, TDHF has been widely used in nuclear physics to study reactions^{19,20}. However, TDHF underestimates the particle correlations, making it a suitable method for describing weakly correlated systems, such as many closed-shell molecules, but unreliable for strongly correlated ones, such as molecules with significant electron-electron interactions. To build correlations on top of TDHF, this framework was extended to the multi-configuration time-dependent Hartree-Fock method (MC-TDHF)^{21–25}. Although these methods are powerful tools for qualitatively capture the behavior of weakly interacting systems, they become unreliable for larger and strongly interacting systems.

With the advancement of computing power and numerical algorithms, interest has resurged in the explicit time propagation of correlated systems. Including electron correlations to predict quantum dynamics beyond mean-field approximations is a challenging task. One often resorts to a class of non-variational methods. For example, only relatively recently has the real-time time-dependent density functional theory (RT-TDDFT) approach been introduced within the local density approximation (LDA) for studying dynamic response properties^{26,27}. Other recent examples are time-dependent versions of multi-configuration self-consistent fields (MC-SCF)^{28–32}, configuration interaction (CI)^{33–39}, algebraic diagrammatic construction^{40–46}, coupled cluster (CC) theories^{35,37,47–56}, dynamical mean-field theory (DMFT)^{57,58}, tensor networks^{59–61} and the density matrix renormalization group (DMRG)⁶². Each of the aforementioned methods faces inherent limitations and/or scalability concerns. Mean-field methods such as DFT and HF encounter difficulties in describing correlation effects as explained above, while CI and CC-based techniques exhibit unfavorable scaling as the size of the system increases⁶³.

Wave-function-based techniques offer the potential for systematically improvable accuracy and precise simulations of electronic eigenstates and are routinely used to capture ground states of electronic systems in continuous space using variational Monte Carlo (VMC). Recently, great progress has been made in the design of variational wave function ansatz, by the introduction of neural quantum states (NQS) with variational Monte Carlo⁶⁴, producing impressively accurate solutions to the electronic TISE^{65–73}. NQS promise to provide high-accuracy wave functions, capturing the entire entanglement of the system, at an affordable computational cost⁶³. However, their application to study quantum dynamics, where correlations are expected to be essential, remains an open problem. Indeed, to the best of our knowledge, there exists no prior work that has successfully extended VMC to capture the real-time evolution of electronic systems in continuous space, despite its possible impact on quantum chemistry and condensed matter.

In this work, we go beyond the mean-field approximation and introduce a novel technique for variational time-dependent wave functions that can capture many-body correlations. We use time-dependent variational wave functions with Jastrow functions and backflow transformations to accurately reproduce the time-dependent wave functions of benchmark experiments, including the solvable harmonic-interaction model, diatomic molecules in an intense laser field, and quenched quantum dots.

Results

Our aim is to capture the time evolution of $|\Psi(t)\rangle$ according to Eq. (2), induced by $\hat{H}(t)$. For electron configurations $x = [\mathbf{r}_1, \dots, \mathbf{r}_N]$ in position space, the Hamiltonian reads

$$\hat{H}(t) = -\frac{1}{2} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 + V(x, t), \quad (3)$$

with time-dependent potential V . We will consider spin-independent Hamiltonians and assume that all electrons have a fixed spin-projection quantum number $\sigma_i \in \{\uparrow, \downarrow\}$.

Variational time evolution

We approximate the time-evolving state $|\Psi(t)\rangle$ using a parametrized Ansatz $|\Phi(\theta(t))\rangle$ with time-dependent parameters $\theta(t) = [\theta_1(t), \dots, \theta_{N_p}(t)]$, reducing the problem to finding the optimal $\theta(t)$ such that $|\Psi(t)\rangle \approx |\Phi(\theta(t))\rangle$. In the Methods section, we illustrate how the trajectories $\theta(t)$ are obtained using the time-dependent variational principle^{18,60,61}. We discuss the generalization of MacLachlan's variational principle into a framework for correlated many-body wave functions, called tVMC, in Methods. This has recently also been demonstrated for bosonic systems^{74,75}, quantum many-body spin systems arising in condensed matter physics^{76–81} and for modeling fermionic lattice Hamiltonians (the Fermi–Hubbard model)⁸². Our work is concerned with its application to ab initio many-electron systems in continuous space, which is relevant to quantum chemistry and condensed matter and which has remained elusive so far. Additionally, in Methods we introduce a novel approach that combines tVMC with Taylor-root expansions to achieve precise evolution of parameterized quantum states, further enhancing the method's capabilities in this new context, especially in conjunction with neural network ansatz.

Time-dependent variational wave-function models

Since the Hamiltonian operator is Hermitian and time-reversal symmetric, one can restrict oneself to real wave functions when solving the static TISE problem⁸³. However, to model quantum dynamics, complex wave functions are generally required. We will introduce variational models in terms of electron positions $[\mathbf{r}_1, \dots, \mathbf{r}_N]$ in a continuous position space. The wave function ansatz must obey the correct permutation symmetry under the exchange of particles, that is, it must be made antisymmetric under electronic permutations. To this end Slater determinants are routinely used, constructed from a set of M complex, time-dependent, single-particle mean field orbitals $\mathcal{M} = \{\varphi_\nu(\mathbf{r})\}_{\nu=1}^M$ (we drop the parameter dependence to simplify the notation). We can go beyond this mean-field approximation and capture many-body correlations using, for example, a complex symmetric Jastrow factor dependent on time $J(x, t)$ that depends on the complete many-body configuration x ⁷⁵. To capture additional correlations and change the nodal surface dictated by the choice of single-particle orbitals, we transform the orbitals into a set of multi-electron orbitals introducing a “time-dependent backflow transformations” (tBF), $\varphi_\mu(\mathbf{r}_i, t) \rightarrow \varphi_\mu^{BF}(\mathbf{r}_i, x, t)$ ⁸². Alternative approaches exist to change the nodal surface, such as the introduction of hidden fermions⁸⁴ and pair-orbitals with Pfaffians or geminals^{85,86}, which can be made time dependent. Hence, our variational time-dependent quantum many-body wave function reads

$$\Phi(x, t) = \det[\varphi_\mu^{BF}(\mathbf{r}_i, x, t)] e^{J(x, t)}. \quad (4)$$

By using time-dependent backflow transformations, our model obtains high expressive power, which allows us to represent states that are significantly more correlated compared to those obtained by mean-field calculations. For a detailed description of the model, we refer to the Supplementary Information. In Fig. 1, we provide a schematic overview of how the time-dependent Jastrow and backflow

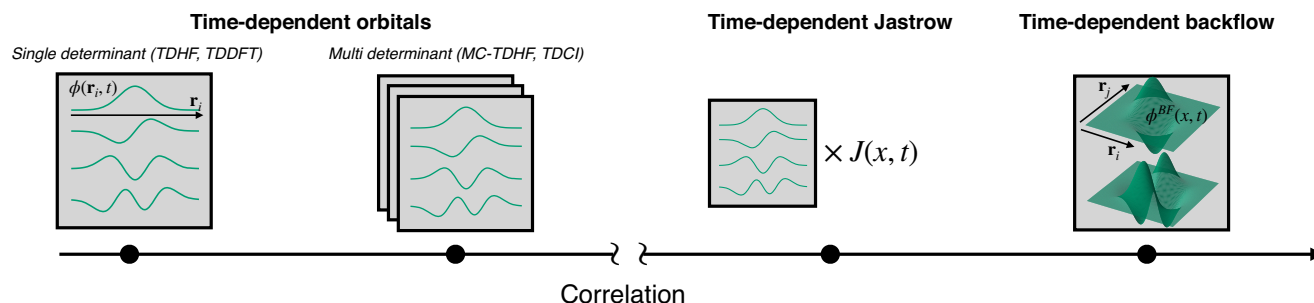


Fig. 1 | Schematic representation of different approaches to capture correlations. Single-determinant approaches with single-particle orbitals are mostly applicable where strong correlations can be neglected. Correlations can be built in using a polynomial number of determinants, a multiplicative time-dependent

Jastrow factor that depends on all the electron positions, or in the most powerful case by using a determinant with higher-dimensional many-body time-dependent orbitals using backflow transformations.

transformations compare with traditionally used time-dependent mean-field approaches.

An alternative and common choice is to forgo the direct description of the wave function in continuous space and introduce a finite basis set. In this case (second quantization), the wave function Ansatz does not need to be constrained to fulfill the correct permutation symmetry, since it is automatically captured by the fermionic creation/annihilation operators and their anti-commutation relations⁸⁷. Instead of positions, states are represented in the occupation number basis $x = [n_1, \dots, n_M]$ (with $n_i \in \{0, 1\}$) for a given set of M mean field orbitals $\mathcal{A} = \{\phi_\mu\}$ (for example, based on Gaussian orbitals or similar). We parameterize $\Psi(n_1, \dots, n_M, t)$ directly with a flexible variational function, such as a neural network, with a set of time-dependent parameters $\theta(t)$, without explicit anti-symmetrization with determinants¹. In particular, we use a complex-valued, time-dependent Restricted Boltzmann Machine (RBM) as in Ref. 64 (see Supplementary Information for details).

Interacting fermions in one dimension

To demonstrate the validity of our approach to capture the time-dependent state of many-body systems, we start with studying the exactly solvable harmonic interaction model in one dimension, describing harmonically confined particles interacting via a harmonic potential:

$$V(x, t) = \sum_{i=1}^N \left[\frac{1}{2} \omega(t)^2 \mathbf{r}_i^2 + \frac{g(t)}{2} \sum_{i>j}^N (\mathbf{r}_i - \mathbf{r}_j)^2 \right], \quad (5)$$

where ω is the trap frequency and $\mathbf{r}_i \in \mathbb{R}$. In particular, we simulate the dynamics of the system subject to a trap quench, for which an analytical solution is known^{88,89}. When the trap frequency is quenched from $\omega_0 \rightarrow \omega_f$ at time $t = 0$, the particles exhibit a breathing mode with period $T = \pi/\omega_f$ for a well-chosen time-dependent interaction strength $g(t)$. In particular, the time-evolved state reads (up to irrelevant global factors)

$$\Psi(x, t) = \det \left[\mathcal{V} \left(\frac{x}{L(t)} \right) \right] e^{-J_{\text{well}}(x, t)} e^{-J_{\text{int}}(x, t)} \quad (6)$$

$$J_{\text{well}}(x, t) = \alpha(t) \sum_{i=1}^N \mathbf{r}_i^2, \quad J_{\text{int}}(x, t) = \beta(t) \left(\sum_{i=1}^N \mathbf{r}_i \right)^2 \quad (7)$$

when $g(t) = g/L(t)^{489}$, with g the original interaction strength at $t < 0$. Here, $\mathcal{V}(x)$ is the Vandermonde matrix, equivalent to a Slater determinant with orbitals $\phi_\mu(\mathbf{r}) = \mathbf{r}^{\mu-1}$, with $\mu = 1, \dots, N$. The time-dependent scale functions $L(t)$, $\alpha(t)$, and $\beta(t)$ can be derived analytically and are given in the Supplementary Information. To study the breathing mode with a variational method, we carry out two experiments to demonstrate that tVMC can capture fermionic time-dependent

correlations: (i) we parameterize $\alpha(t)$, $\beta(t)$, $L(t)$ with time-dependent constants, and (ii) we represent the correlation contribution to the Jastrow J_{int} with a neural quantum state (NQS) Ansatz. For the latter, we use two general DeepSet neural network architectures (as introduced in ref. 90 to model bosonic ground states), one for $\text{Re}[J_{\text{int}}]$ and one for $\text{Im}[J_{\text{int}}]$, with time-dependent parameters. This choice of architecture guarantees the particle-permutation invariance of the Jastrow factor. In Fig. 2 we compare the evolution of the monopole $Q = \sum_i^N \langle \mathbf{r}_i^2 \rangle$ as a function of time for 30 fermions and $\omega_0 = 1 \rightarrow \omega_f = 2$ and $g = 1$, using the parameterizations mentioned above. We observe that the breathing mode and correlations are both accurately reproduced with the tVMC method, thus validating our approach.

Molecules in a laser field

As a more complex case study, we focus on the electronic response of a diatomic molecule in an intense, time-dependent laser field. The electronic potential with N_A atoms at positions $\{\mathbf{R}_a\}_{a=1}^{N_A}$ reads (in atomic units)

$$V(x, t) = \sum_{i>j}^N \frac{1}{\|\mathbf{r}_i - \mathbf{r}_j\|} - \sum_i^N \sum_a^{N_A} \frac{Z_a}{\|\mathbf{r}_i - \mathbf{R}_a\|} + V_{\text{ext}}(x, t) \quad (8)$$

where we introduce the charge number Z_a and an external potential $V_{\text{ext}}(x, t)$ describing a linearly polarized and spatially homogeneous electric field (see ref. 20 and the Supplementary Information for details). Hartree-Fock is known to be unable to properly describe the dissociation curve of H_2 , especially at large distances⁹¹. Therefore, we will consider H_2 separated by twice its equilibrium distance. In Fig. 3 we show the induced dipole moment for H_2 modeled in both the first and second quantization formalism. We include TD-HF and Exact Diagonalization (ED) results in the minimal basis set STO-3g where the number of orbitals is equal to the number of electrons. Here, 3 Gaussian primitive functions are used to approximate each Slater-type orbital. Since the electric field induces an increased delocalization of the orbitals, we show results for TD-HF and ED in a larger basis set cc-pVDZ, which includes correlation-consistent polarized valence basis sets and uses successively larger shells of polarization (correlating) functions.

The initial state of the various approaches is their respective approximation to the ground state of H_2 , which slightly differ depending on the accuracy of the method. The ground state results are summarized in the Supplementary Information. The effect of correlations (i.e. ED versus HF predictions) can be observed mainly in oscillation amplitudes, as well as the interference behavior superimposed on the electric-field-induced oscillatory behavior. In contrast to TD-HF in the same basis set, tVMC with tNQS reproduces the ED results, thereby demonstrating that tNQS can accurately capture the electron correlations, even in a limited basis set. In continuous space, we use a

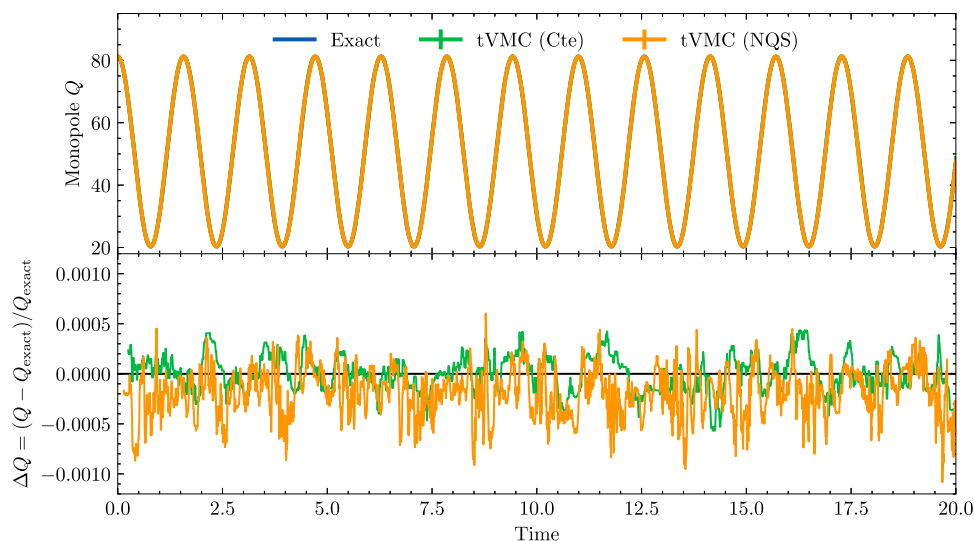


Fig. 2 | Monopole Q for the harmonic interaction model with 30 particles, subject to a quench of the harmonic confinement and a time-dependent interaction strength. (top panel) We show the predictions with tVMC using the (i) time-dependent constants Ansatz in green, and (ii) the neural quantum state in

orange, both introduced in the main text. We compare to the exact solution in blue. The curves are overlapping and therefore hardly distinguishable. (bottom panel) The relative error ΔQ on the predicted monopole, averaged over a rolling window of $\Delta t = 0.2$ to reduce the effect of statistical noise.

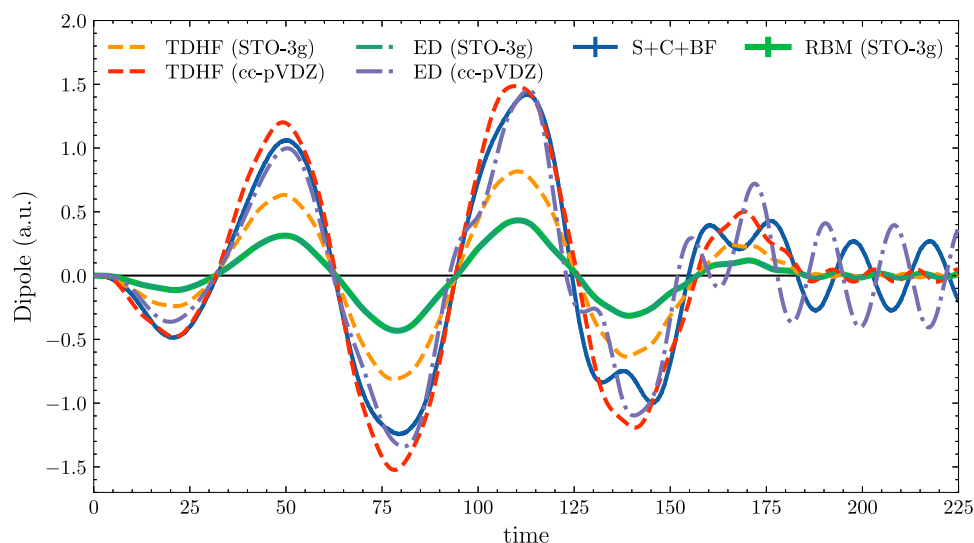


Fig. 3 | Time-dependent dipole moment of H_2 in an intense, time-dependent laser field. Time-dependent dipole results using an NQS and tVMC. We show the effect of capturing correlations with a Slater determinant with time-dependent

neural backflow transformation and a Jastrow representing the cusp condition (S+C+BF), as well as results obtained in the STO-3g basis in second quantization (RBM). We compare to predictions from TDHF and ED.

neural network ansatz, inspired by PauliNet⁶⁶ and neural backflow transformations⁹², using a modified version of the powerful particle-attention backflow transformations recently introduced in Ref. 68 for applications to the homogeneous electron gas. The latter has recently also found successful applications to quantum materials⁹³ nuclear matter⁹⁴, and ultra-cold dilute matter⁹⁵. The details of the model are given in the Supplementary Information. First, as a validation, we observe that tVMC with a pure mean-field Slater determinant reproduces the predictions from TD-HF in the same basis, although tVMC scales more favorably with the size of the basis set, i.e. $\mathcal{O}(M)^3$ compared to $\mathcal{O}(M^4)$ (see Supplementary Information for more details on scalability). By including a time-dependent backflow and therefore electron correlations, the time evolution of the dipole changes compared to mean field, which prominently manifests itself as a damping effect on the oscillations. The resulting time-dependent electron densities have been visualized in Supplementary Movie 1.

Quenched electronic quantum dot

As a final demonstration of the capabilities of our method, we model the behavior of confined electrons in two dimensions, within a harmonic well. This system, also known as a quantum dot, describes electrons propagating in a semi-conducting material. It exhibits intensified Coulomb interactions due to a strong dielectric confinement^{95–97}, which influence crucial optoelectronic properties^{98–101}. The simulation of these Coulomb-induced correlations is vital for describing these properties^{12,102–104} and the system therefore serves as an ideal test-bed to compare to less expressive mean-field methods.

The interaction and confining potential in this system reads

$$V(x, t) = \sum_{i=1}^N \frac{1}{2} \omega^2 \mathbf{r}_i^2 + \sum_{i,j}^N \frac{\kappa(t)}{\|\mathbf{r}_i - \mathbf{r}_j\|}, \quad (9)$$

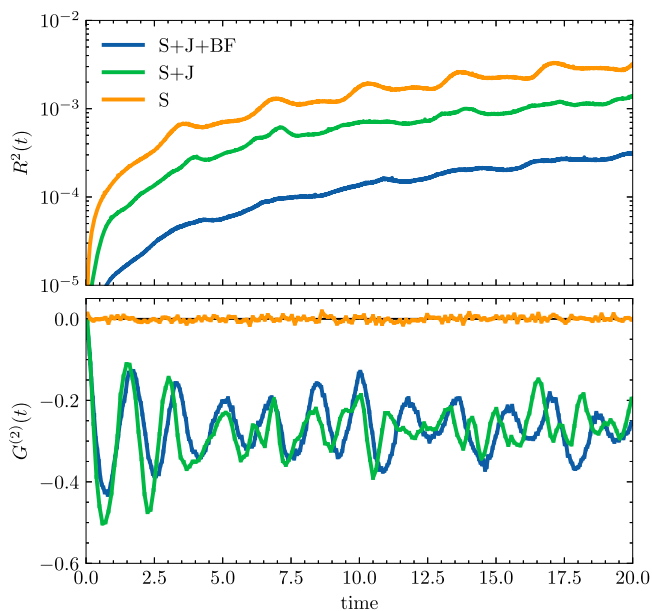


Fig. 4 | Correlations in a quenched quantum dot. The integrated $R^2(t)$ error in Eq. (20) (top panel) and pair correlation $G^{(2)}(t)$ in Eq. (22) (bottom panel) as a function of time for a fully polarized quantum dot with $N = 6$ and subject to a quench $\kappa(t) = 1 \rightarrow 2$ at $t = 0$. We compare with predictions using tVMC with a single Slater determinant (S), a Slater-Jastrow model (S+J), and a Slater-Jastrow-Backflow (S+J+BF) model.

where ω is the trap frequency, and $\kappa > 0$ is the interaction strength¹², related to the dielectric constant of the semiconductor¹⁰⁵. We consider the evolution of the electronic ground state of the Hamiltonian with $\kappa(t < 0) = 1$ after a quench that induces a sudden screening of the mutual Coulomb interaction due to a change in the static dielectric constant of the semiconductor. The latter is modeled by an abrupt doubling of the effective interaction strength $\kappa(t \geq 0) = 2$ at $t = 0$, while fixing the confining potential $\omega = 1$.

Although one can again observe breathing modes in the electric monopole (see Supplementary Fig. 4), we focus here on observables that specifically highlight the correlations in the system. To highlight the effect of correlations in this system, we include the connected pair-correlation function $G^{(2)}$ in Fig. 4, which isolates correlation effects and is identically zero in the mean-field limit (see Eq. (22) for the definition). We observe that, even though correlations do not have a quantitative effect in the ground state, they significantly contribute shortly after the quench and remain present throughout the time evolution. In Fig. 4 we also show the integrated error measure R^2 , introduced in Eq. (20) to quantify the degree to which the models satisfy the TDSE. We conclude that a more expressive wave function also yields significantly lower integration errors and is therefore closer to the exact solution of the time-dependent Schrödinger equation. The presence of correlations explains the rapid increase in integration error for the mean-field model in Fig. 4, as the latter does not capture the strong correlations induced by the change in interaction strength. Furthermore, allowing the nodal surface to vary over time (using backflow transformations) yields more accurate and truthful dynamics.

We also demonstrate the use of neural quantum states to capture the correlated electronic time-dependent wave function of the quantum dot quench. To this end, we use a novel higher-order method, called tre-tVMC (see Methods). In Fig. 5, we compare the integration error for an NQS ansatz with the basis-expanded wave function for $N = 6$ (see Supplementary Information for model details). We observe that the NQS-based ansatz is more expressive due to the flexible neural orbitals, and better captures the electron correlations through the neural Jastrow factor. We also show the results for larger systems up to

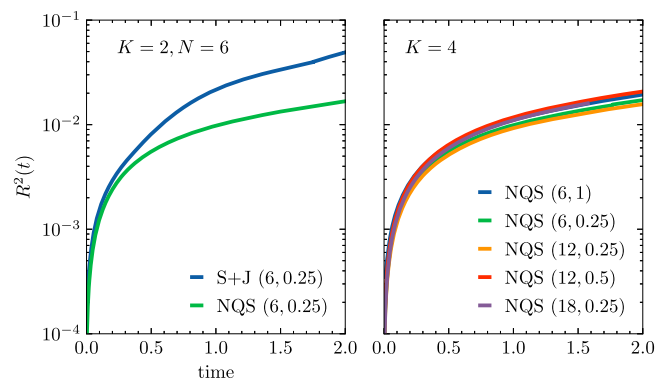


Fig. 5 | Accuracy of quenched quantum dots dynamics with varying system sizes. The integrated R^2 for a fully polarized quantum dot with $N = 6$ and subject to a quench $\kappa(t) = 1 \rightarrow 2$ at $t = 0$ (see also Supplementary Fig. 4), using the tre-tVMC approach with given order K . Between brackets, we indicate the number of electrons and the time step: $(N, \delta t \times 10^2)$. We compare the results using the basis expanded Slater-Jastrow model (S+J) with $K = 2$ TRE to a fully neural-network-based wave function ansatz (NQS).

$N = 18$ electrons, using the higher-order Taylor-root expansion scheme with a local error $\mathcal{O}(\delta t^5)$ (denoted $K = 4$). This demonstrates that our approach yields accurate results for various system sizes. The largest many-electron system of $N = 18$ fermions is shown in more detail in Fig. 6 where we observe strong variations in the single-body density over time. Hence, during the quench the delocalization of the orbitals oscillates, thereby suggesting that wave function models without basis dependence are most appropriate to capture the time-dependent wave function of the electron systems.

Discussion

We have introduced a variational approach to capture the dynamics of quantum many-electron systems, specifically addressing the challenges posed by real-time ab initio electron dynamics. Our methodology involves the use of correlated time-dependent variational wave functions, which surpass the typically adopted mean-field approximations. In particular, we adopted here the time-dependent Jastrow function and the backflow transformation to capture electronic correlations. We discussed how to time-evolve the variational wave functions using the time-dependent variational Monte Carlo (tVMC).

We demonstrated the effectiveness of our approach through applications to three distinct systems: the solvable harmonic interaction model, diatomic molecules in intense laser fields, and a quenched quantum dot. In the harmonic interaction model, we successfully reproduced the breathing mode induced by a trap quench, underscoring the method's accuracy in capturing correlated many-body system dynamics. Transitioning to diatomic molecules in intense laser fields, our approach demonstrated versatility in both first and second quantization. In both cases, we demonstrated that tVMC can be used to time-evolve expressive models such as Neural Quantum States, as well as the more traditional basis-expanded models. We also introduce a novel alternative to tVMC, called tre-tVMC, that is particularly powerful when using expressive neural-network wave functions in continuous space. In first quantization, the incorporation of neural backflow transformations showcased a promising avenue for simulating complex molecular systems in external fields. Finally, our approach excelled in predicting observables for the quenched quantum dot, emphasizing the significance of capturing many-body correlations in the dynamics of strongly interacting electronic systems. In conclusion, our variational time-dependent wave function approach, as demonstrated across different systems, presents a promising direction for advancing real-time electron dynamics, offering a balance between

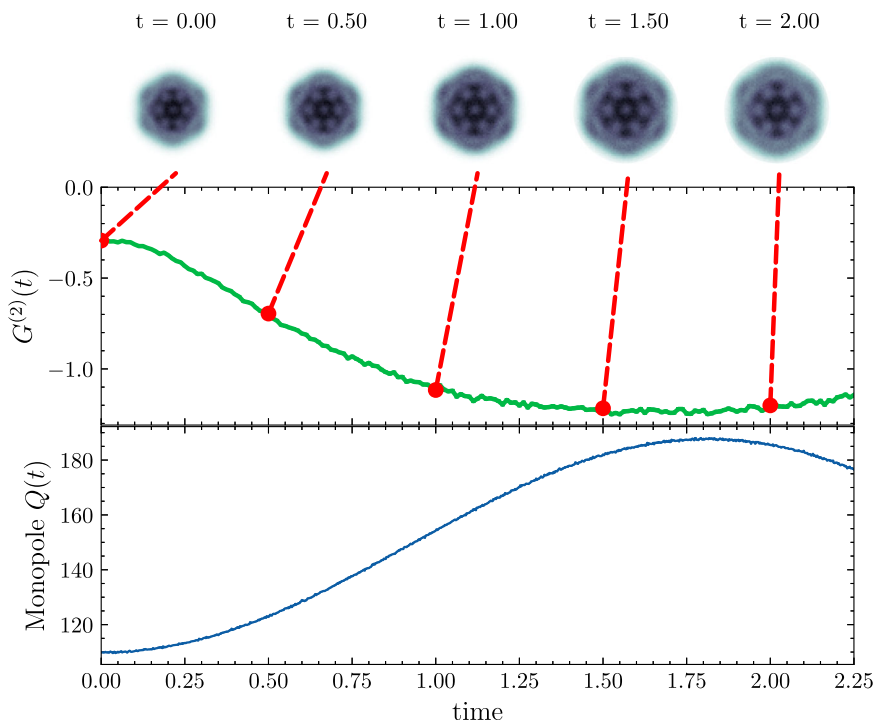


Fig. 6 | Observables for a quenched quantum dot with 18 electrons. Integrated pair correlation $G^{(2)}(t)$ and monopole $Q(t)$ as a function of time. We show the results obtained with the NQS wave function for the 2d quantum dot with $N = 18$ electrons (see Fig. 5). In the top row, we show snapshots of the single-body density $\rho(\mathbf{r})$.

accuracy and computational efficiency in capturing the intricate dynamics of quantum many-electron systems.

The presented work opens avenues for further exploration and improvement. One avenue is the extension of our approach to larger and more complex systems. Additionally, exploring more powerful ansatzes may provide further improvements in accuracy and efficiency. Furthermore, the applicability of our method to more diverse quantum many-electron systems, including materials and chemical reactions, could uncover new insights into their dynamic behaviors.

Methods

Variational time evolution with TDVP

The time evolution of a state $|\Phi(\theta(t))\rangle$ over a small time interval δt described by the TDSE can be approximated as $|\tilde{\Psi}(t + \delta t)\rangle = (1 - i\delta t\hat{H})|\Phi(\theta(t))\rangle$. A variational approach projects $|\tilde{\Psi}(t + \delta t)\rangle$ back onto the trial state manifold or requires finding the $\theta(t + \delta t)$ that optimally approximates the state evolved in time. These approaches are known as “time-dependent variational principles” (TDVP). Various methods are available for this projection and include the Dirac-Frenkel (DF) and MacLachlan (McL) variational principles. In particular, McL reduces to DF for holomorphic wave function parameterizations. However, in general, DF conserves the energy of the system subject to time-independent Hamiltonians, in contrast to the non-symplectic McL approach. For a discussion and comparison of the various TDVPs available, we refer to refs. 106–108. Furthermore, explicit projection methods have recently been introduced^{78,80,109}. For simplicity, we will assume in this section that all parameters are complex and the wave function Ansatz is holomorphic. We minimize the (Fubini-Study) distance between the time-evolved state $|\tilde{\Psi}(t + \delta t)\rangle$ and the parametrized state $|\Phi(\theta(t + \delta t))\rangle$, setting $\theta(t + \delta t) = \theta(t) + \dot{\theta}(t)\delta t$ for small time-steps δt , to obtain a first-order differential equation for the variational parameter velocities $\dot{\theta}$,

$$\sum_k^{N_p} G_{k,k'}(t) \dot{\theta}_{k'}(t) = -iF_k(t), \quad (10)$$

with the Quantum Geometric Tensor G (QGT) and the energy gradients F given by

$$G_{k,k'}(t) = \left\langle \frac{\partial}{\partial \theta_k} \Phi(\theta(t)) \middle| \frac{\partial}{\partial \theta_{k'}} \Phi(\theta(t)) \right\rangle, \quad (11)$$

$$F_k(t) = \left\langle \frac{\partial}{\partial \theta_k} \Phi(\theta(t)) \middle| \hat{H}(t) \middle| \Phi(\theta(t)) \right\rangle. \quad (12)$$

Time-dependent variational Monte Carlo (tVMC)

Although MacLachlan’s and Dirac-Frenkel’s variational principle were originally introduced in conjunction with mean-field states, one can generalize the approach to incorporate many-body correlations. Therefore, we formulate the variational time evolution using Monte Carlo estimates to integrate the system over the exponentially large Hilbert space, as we will demonstrate in this section. We aim to capture the dynamics of the probability amplitudes $\Psi(x, t) \equiv \langle x | \Psi(t) \rangle \in \mathbb{C}$, which we parameterize as $\Phi(x, \theta(t)) \equiv \langle x | \Phi(\theta(t)) \rangle$. Here, x represents a set of continuous electron positions and spins, or an occupation configuration in a given basis set. Since the Hilbert space scales exponentially with the system size, we resort to Monte Carlo estimates of the quantities in Eqs. (11) and (12). The time-dependent variational principle in combination with Monte Carlo is referred to as time-dependent Variational Monte Carlo (tVMC)^{75,91,110}. For a given trial wave function, the energy can be computed using (we drop the time dependence to simplify the notation),

$$E = \mathbb{E}_{x \sim |\Phi(x, \theta)|^2} [E_{\text{loc}}(x)], \quad (13)$$

where we introduced the local energy $E_{\text{loc}}(x) = \frac{[\hat{H}\Phi](x, \theta)}{\Phi(x, \theta)}$. Furthermore, by introducing the log derivative of the wave function with respect to parameter θ_k : $O_k(x) = \partial_{\theta_k} \log \Phi(x, \theta)$, we obtain the following

estimators

$$G_{k,k'} = \mathbb{E}_{x \sim |\Phi(x, \theta)|^2} [O_k^*(x) \Delta O_{k'}(x)], \quad (14)$$

$$F_k = \mathbb{E}_{x \sim |\Phi(x, \theta)|^2} [O_k^*(x) \Delta E_{\text{loc}}(x)], \quad (15)$$

where $\Delta E_{\text{loc}}(x) = E_{\text{loc}}(x) - E$ and $\Delta O_k(x) = O_k(x) - \mathbb{E}_{x' \sim |\Phi(x', \theta)|^2} [O_k(x')]$. We refer to the Supplementary Information for more details.

After estimating the energy derivatives and quantum geometric tensor using Eqs. (15) and (14), we solve the linear system of equations in Eq. (10) using the regularized singular value decomposition introduced in refs. 81,111. An unbiased estimate of the QGT and a stable and accurate inversion of the latter is essential to time-evolve the parametrized state with tVMC, and can become challenging in the large-parameter limit relevant for highly expressive neural-network-based wave functions. For this reason, in the next section we introduce a complementary approach more suitable when considering such regime.

Taylor-root expansion tVMC (tre-tVMC)

We introduce an additional method to evolve a parametrized quantum state using variational Monte Carlo. Our central goal is again to maximize the fidelity between the true time-evolved state $|\Psi(t + \delta t)\rangle$, and a state on the variational manifold $|\Phi(\theta)\rangle$. For this task, we first consider a Taylor expansion consistent to order K in δt . Rather than evaluating higher orders in $\hat{H}$ directly (which is computationally expensive, especially in continuous space), we compute these through sequential optimizations. One possible approach is to variationally compress the states in the Krylov basis $\{1, \hat{H}, \hat{H}^2, \dots\}|\Psi(t)\rangle$, yet this proves challenging in practice, since these basis states are significantly different from the initial reference state $|\Psi(t)\rangle$. A more convenient method is to target intermediate states that are at most $\mathcal{O}(\delta t)$ different from $|\Psi(t)\rangle$, thereby greatly reducing the computational burden. With this idea in mind, we factorize the time evolution operator as

$$e^{-i\delta t \hat{H}} = \prod_{k=1}^K \hat{R}_k + \mathcal{O}(\delta t^{K+1}), \quad (16)$$

and set $\hat{R}_k = 1 - ic_k \delta t \hat{H}$ with constants $c_k \in \mathbb{C}$ to be determined. The latter can be obtained by equating Eq. (16) to the Taylor expansion of the propagator. In other words, we rewrite the propagator in terms of the roots of the Taylor polynomials associated with the exponential function (which we refer to as the *Taylor roots expansion*)¹¹². For example, for $K = 2$ this results in $c_k = (1 \pm i)/2$. Hence, we sequentially optimize the fidelity for the evolution operators

$$\hat{R}_1 = 1 - i\delta t \left(\frac{1+i}{2}\right) \hat{H}, \quad \hat{R}_2 = 1 - i\delta t \left(\frac{1-i}{2}\right) \hat{H}. \quad (17)$$

In practice, we obtain a first set of optimal parameters θ_1^* by optimizing $\mathcal{F}(\hat{R}_1|\Psi(t)\rangle, |\Phi(\theta_1)\rangle)$, and sequentially obtain a second set of parameters θ_2^* by optimizing $\mathcal{F}(\hat{R}_2|\Phi(\theta_1^*)\rangle, |\Phi(\theta_2)\rangle)$, resulting in a state $|\Phi(\theta_2^*)\rangle$ that approximates $|\Psi(t + \delta t)\rangle$ consistently to second order in δt : $|\Psi(t)\rangle \xrightarrow{\hat{R}_1} |\Phi(\theta_1^*)\rangle \xrightarrow{\hat{R}_2} |\Phi(\theta_2^*)\rangle \approx |\Psi(t + \delta t)\rangle$. The latter yields an integration consistency similar to the Heun integration scheme. Higher-order integrators can easily be obtained in a similar way by solving Eq. (16) for higher K (for a more detailed discussion, we refer to the Supplementary Information). We optimize the fidelity using the MC estimator discussed in the Supplementary Information, where we also introduce a set of useful tricks to accelerate the evolution and optimization.

With this approach and for a fixed time step δt , we can now simulate the dynamics of a quantum state consistently to order δt^K at K times the computational cost as a first-order approach (corresponding to $K = 1$ with $c_1 = 1$). We dub this method “tre-tVMC”, for Taylor roots

expansion tVMC. Our approach improves the stability of the time evolution by avoiding using the TDVP principle, which requires an accurate inversion of the QGT. Therefore, the method is more suitable in the large-parameter regime where it can be turned into a method that scales linearly with the number of parameters involved¹¹³. On the other hand, every time step requires a set of optimizations that can render tVMC significantly more efficient for smaller models.

Other options than the Taylor expansion are, in principle, possible. For example, ref. 80 considered Trotter expansions which yield a set of unitary operators, thereby simplifying the fidelity estimator for each Trotter factor. However, in MC the operators in the Trotter expansions must be estimated sequentially for each time step, which induces a scaling with the number of particles involved and therefore limits the time evolution to smaller system sizes. Furthermore, Trotterization is significantly more involved for ab initio continuous-space Hamiltonians with unbounded potentials, such as the Coulomb potential¹¹⁴. Additionally, by evolving with operators containing the full Hamiltonian $\hat{H}$, we can also maintain the symmetry of the Hamiltonian in time.

Integrated infidelity

We can estimate the error induced by the restricted capability of the variational model to represent $|\Psi(t + \delta t)\rangle$, by introducing the residuals^{64,77}

$$r^2(t) = \mathcal{D}^2(|\Psi(t + \delta t)\rangle, |\Phi(\theta(t + \delta t))\rangle) / (N\delta t)^2 \quad (18)$$

$$\approx N^{-2} [\text{Var}_{\Phi(\theta(t + \delta t))}(\hat{H}) + \hat{\theta}^\dagger G \hat{\theta} + 2 \text{Im}(\hat{F}^\dagger \hat{\theta})], \quad (19)$$

where $\mathcal{D}(|\Psi\rangle, |\Phi\rangle)$ represents the Fubini-Study distance between quantum states $|\Psi\rangle$ and $|\Phi\rangle$, and the last line is obtained through a second-order consistent expansion in $\hat{\theta}$ and $\text{Var}_{\Psi}(\hat{H}) = \mathbb{E}_{x \sim |\Psi|^2} [E_{\text{loc}}^*(x) \Delta E_{\text{loc}}(x)]$. Furthermore, we introduce the integrated fidelity

$$R^2(t) = \int_0^t dt' r^2(t'). \quad (20)$$

Pair correlation function

To identify beyond-mean-field correlations, we introduce a pair-correlation function that vanishes for pure mean-field states. We introduce the pair correlation function for a general state $|\Psi\rangle$ (with position vectors $\mathbf{x} \neq \mathbf{y} \in \mathbb{R}^d$, and assuming a fully polarized system such that we can ignore spin)

$$\begin{aligned} g^{(2)}(\mathbf{x}, \mathbf{y}) &= \langle \Psi | \phi^\dagger(\mathbf{x}) \phi(\mathbf{x}) \phi^\dagger(\mathbf{y}) \phi(\mathbf{y}) | \Psi \rangle / \mathcal{N} \\ &\quad - \langle \Psi | \phi^\dagger(\mathbf{x}) \phi(\mathbf{x}) | \Psi \rangle \langle \Psi | \phi^\dagger(\mathbf{y}) \phi(\mathbf{y}) | \Psi \rangle / \mathcal{N}^2 \\ &\quad + \langle \Psi | \phi^\dagger(\mathbf{x}) \phi(\mathbf{y}) | \Psi \rangle \langle \Psi | \phi^\dagger(\mathbf{y}) \phi(\mathbf{x}) | \Psi \rangle / \mathcal{N}^2. \end{aligned} \quad (21)$$

where $\mathcal{N} = \langle \Psi | \Psi \rangle$ is the normalization, and where we introduced the field creation and annihilation operators $\{\phi^\dagger(\mathbf{x}), \phi(\mathbf{x})\}$ at position $\mathbf{x}$. We define the fully integrated pair correlations function as

$$G^{(2)} = \int d\mathbf{x} d\mathbf{y} g^{(2)}(\mathbf{x}, \mathbf{y}). \quad (22)$$

We obtain the Monte Carlo estimator (see Supplementary Information for a detailed derivation)

$$G^{(2)} = N^2 \mathbb{E}_{x \sim |\Psi|^2} \left[\frac{\Psi(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N)}{\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}'_N)} - \frac{1}{N} \right]. \quad (23)$$

For a mean-field state, the pair-correlation function vanishes $G^{(2)} \equiv 0$.

Data availability

Source data for the figures has been deposited in Figshare under accession code <https://doi.org/10.6084/m9.figshare.27102529>⁴⁵.

Code availability

The simulations in this work were carried out using NetKet^{116,117}, which relies on Jax¹¹⁸, and MPI4Jax¹¹⁹. For the molecular system, we used PySCF¹²⁰ for benchmarking purposes and to construct the Hamiltonian in second quantization. The code implementing the tre-tVMC approach is publicly available <https://github.com/cqsl/tre-tVMC> and Ref. 121. The models and observables can be found on the project's GitHub page <https://github.com/cqsl/electron-tvmc> and Ref. 122.

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Author contributions

J.N. wrote the code and ran the experiments. All authors contributed to the design of the methods, discussed the results, and wrote the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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