Multistate transition dynamics by strong time-dependent perturbation in NISQ era

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Abstract
We develop a quantum computing scheme utilizing McLachlan variational principle in a hybrid quantum–classical algorithm to accurately calculate the transition dynamics of a closed quantum system with many excited states subject to a strong time-dependent perturbation. A systematic approach for optimal construction of a general $N$-state ansatz with unary $N$-qubit encoding is refined. We also use qubit efficient encoding in McLachlan variational quantum algorithm to reduce the number of qubits to $\log_2 N$, simultaneously diminishing depths of the quantum circuits. The significant reduction of the number of time steps is achieved by use of the second order marching method. Instrumental in obtaining high accuracy are adaptations of the circuits to include time-dependent global phase correction. We illustrated, tested and optimized our quantum computing algorithm on a set of 16 bound hydrogenic eigenstates exposed to a strong laser attosecond pulse. Results for transition probabilities are obtained with accuracy better than 1%, as established by comparison to the benchmark data. Use of interaction representation of the Hamiltonian reduces the noise accumulation while the quantum system evolves in time.

1. Introduction

All physical and chemical phenomena and reactions in the Universe are undergoing constant changes, at their characteristic time scales. Simulation of dynamic systems, significant in comprehending the nature, is hence considered as one of the most important and promising applications of quantum computers. Since Feynman proposed the idea of simulating many-body dynamics using quantum computers [1], various approaches have been explored over the last few decades to provide the insight of physics beyond the reach of classical computers [2–5]. The efforts of existing work in quantum computing are mainly focused on the static [6–10] and dynamical [9–13] properties of many-body systems. Quantum algorithms developed for quantum computing, such as the quantum phase estimation [14] and HHL algorithm [15] often require large circuit depth, which consequently demands a quantum device with qubits of high fidelity and long coherence time for the successful execution, mainly not available in the Noisy Intermediate-Scale Quantum (NISQ) hardware [16]. This has encouraged development of Variational Hybrid Quantum–Classical algorithms (VHQCs) [17–25] which show respectable successes. The general framework for VHQCs is characterized by shallow quantum variational circuits followed by postprocessing with classical computational techniques. The VHQCs have applications in a wide range of quantum computing problems during the NISQ era, such as the Variational Quantum Eigensolver (VQE) [17, 26], Quantum Approximate Optimization algorithm (QAOA) [18, 27], and Variational Quantum Linear Solver (VQLS) [22, 28].

In quantum physics and chemistry, there are two classes of computationally difficult problems: (1) the eigenvalue problem of a many-body systems, including excited states, and (2) the time evolution of a quantum system, including transition dynamics between multitude of excited states. The challenge we have in mind is to develop and apply a quantum algorithm, that can evolve and atomic system with controlled accuracy (<1%)
under a strong time-dependent perturbation which causing transitions between many system states. This problem is formidable even for a few-body system. We successfully answer the challenge at an example of hydrogen atom in a strong, attosecond laser field pulse, to focus on and stress the important properties and difficulties of calculating accurate transitions between fully entangled many-fold of electronic states, subject to strong, attosecond, time dependent perturbation. We tested the algorithm using a quantum simulator, reaching the desired accuracy.

The time-dependent problems are computationally much more involved than the static ones, owing to a need to apply the calculations consecutively for many time steps as the system evolves. The number of the steps could be exceedingly large due to accuracy requirements when a large number of small time steps is used to describe the full system evolution. Simultaneously, one must keep the propagation of the numerical error at minimum, so that the final probabilities for all states of interests reach accuracy at an acceptable level (which we set to be <1%) defined by the deviation from the benchmark.

There is a number of publications treating the quantum computing aspects of the time-dependent transition dynamics in quantum systems using the trotterization of the evolution operator \( e^{-i\mathbf{H}t} \) [29–32]. The theory of VHQCAs for a quantum computer simulation of the general real- and imaginary-time evolution has been established in [19], and developed in various aspects [20, 33, 34]. Error minimization by extrapolation to zero was introduced to VHQCAs in [19] for the quantum Ising model of three spins initialized in the cluster state, with significantly suppressed effect of errors. Adaptive expansion of ansatz was applied to VHQCAs for dynamical simulation of the finite-rate quantum quench in the integrable Lieb-Schultz-Mattis spin chains and sudden quench of the nonintegrable mixed-field Ising model [35]. This resulted in a highly accurate results and much shallower circuits with two orders of magnitude smaller number of CNOT gates comparing to the first-order trotterization method. Furthermore, VHQCAs were extended to the generalized time evolution with a non-Hermitian Hamiltonian and open quantum system dynamics [33]. This was applied to simulation of the ideal and dissipative evolution of 2D Ising model, which showed good agreement with exact solutions. However, as far as we know, none of the implementations of VHQCAs has been developed for a near-term quantum computer to accurately simulate transitions in a fermionic dynamic system to a number of excited states by a strong, time-dependent perturbation.

In this work, we apply VHQCA based on McLachlan’s variational principle (MLVP) [36] to solve transition dynamics of a closed, quantum system with potentially many excited states subject to a strong time-dependent perturbation. We apply and test quantum circuits applicable in quantum computers to calculate excitation dynamics using an example of a single-electron atom in a strong, attosecond laser field pulse in dipole approximation within a multitude of 16 hydrogenic states. Our contributions in this work can be summarized as following: (1) We propose a systematic approach to construct a general \( N \)-state ansatz to be used in unary encoding, using Jordan-Wigner encoding (JWE) [34, 37, 38] and \( N \) qubits, capable to reach highly accurate transition probabilities by controlling the time-step size; (2) We apply a compact encoding method, so called qubit efficient encoding (QEE) [29, 30, 39, 40] in McLachlan VHQCA to simulate the evolution of a system affected by a strong, time-dependent perturbation, reducing the number of required qubits from \( N \) in unary encoding to \( \log_2 N \), and significantly lessening the circuit depth; (3) The second-order parameter marching method is applied reducing the simulation time by an order of magnitude; (4) A model of quantum noise is used in simulation to investigate the error accumulation and an approach to reduce the error accumulation; (5) All results obtained by simulation of our quantum algorithm are compared with accurate benchmark results obtained by the classical algorithms to provide verification of the successful choice of the computational parameters and propose optimal computational techniques for reaching deviations less than 1%.

The details on the VHQCAs developed in this work and resulting quantum circuits are shown in section 2. The results, tests and discussions using different encoding techniques are presented in section 3. The performance of the developed quantum algorithms in presence of a noise model and sampling errors is discussed in section 4. Finally, our conclusions are given in section 5. All mentioned abbreviations are listed in table 1

2. Methods

2.1. General approach

In general, a dynamic atomic quantum system is described by the Time Dependent Schrödinger equation (TDSE) which defines the time evolution of the system wavefunction \( \psi(r, t) \) (atomic system of units, \( \hbar = m = e = 1 \), is used throughout this manuscript, unless otherwise said):
The hydrogen atom is exposed to a short and strong laser pulse. The interaction energy of the electron with the classical, linearly polarized dipole laser field in the length gauge is defined by:

\[
P(r, t) = F(t) \cdot r
\]

where

\[
F(t) = F(t) \hat{z}
\]

\[
F(t) = E(t) \cos(\omega t)
\]

and the time-dependent amplitude of electric field has Gaussian switching conditions:

\[
E(t) = E_0 e^{-\frac{(t-t_0)^2}{2\sigma^2}}
\]

with Full Width at Half Maximum (FWHM) = 2(ln 2)\frac{1}{\sqrt{2}} \tau. The unperturbed Hamiltonian \(H_0(r)\) in this case is the standard hydrogen Hamiltonian \(H(r) = -\frac{\hat{p}^2}{2m} + V(r)\), where \(V(r) = -\frac{1}{r}\) is the potential energy of electron.

The hydrogen excited states in the truncated basis are all with \(m=0\) magnetic quantum number when one starts from the initial state 1s, and follow the optical selection rules with a linearly polarized laser, \(\Delta l = \pm 1\), \(\Delta m = 0\). The sets of the hydrogenic orbitals used to define the model atom are listed in section SI of Supplemental Material (SM).

We choose \(E_0 = 0.25\), \(\tau = 20.5\), \(t_0 = 50\) in equation (5). The laser will reach its maximum amplitude at about \(t \sim 50\), and is considered to be practically zero at \(t \sim T = 200\). This enables calculation of the \(S\)-matrix elements for the transition of the atom from initial state defined before the laser is switched on at \(t = 0\) to a final state after the laser is switched off at \(t = T\) [44].

While previous works have explored various types of ultrashort pulses [45–47], our study specifically focuses on two distinct frequencies, denoted as \(\omega\), as depicted in equations (4b). This selection allows us to generate two characteristic and very strong time-dependent perturbing fields, as illustrated in figure 1, with FWHM≈825.7 as. For \(\omega = 0.06\) (wavelength \(\lambda \sim 700\) nm, i.e. single photon energy about 1.63 eV), we created a unipolar half cycle pulse (UHCP) which has recently been recognized [48, 49] as potentially effective tools for controlling atomic processes at atomic time scales and have been experimentally realized using different approaches, such as the conversion of bipolar to unipolar pulses in thin films [50]. Modeling unipolar HCPs is also of interest in ion-atom collisions, particularly when employing the impact parameter approximation (explained in detail in

### Table 1. List of abbreviations.

| Abbreviation | Description |
|--------------|-------------|
| NISQ         | Noisy intermediate-scale quantum |
| VHQC         | Variational hybrid quantum–classical algorithm |
| VQE          | Variational quantum eigensolver |
| QAOA         | Quantum approximate optimization algorithm |
| VQLS         | Variational quantum linear solver |
| MLVP         | McLachlan's variational principle |
| JWE          | Jordan-Wigner encoding |
| QEE          | Qubit efficient encoding |
| TDSSE        | Time dependent Schrödinger equation |
| FWHM         | Full width at half maximum |
| HCP          | Half cycle pulse |
| ODE          | Ordinary differential equations |
| GPC          | Global phase correction |
| FOM          | First-order marching |
| SOM          | Second-order marching |
| AB2          | Adams-Bashforth second order |
| SR           | Schrödinger representation |
| IR           | Interaction representation |

\[
\frac{\partial \psi(r, t)}{\partial t} + iH(r, t)\psi(r, t) = 0
\]
section SIII.C of SM). In our case, we approximate UHCP by a Gaussian envelope. For example, a HCP-like electric field appears as the orthogonal component of electric field in electron-ion collisions. A unipolar HCP in general can be approximated by Dirac delta function if the pulse is short enough [51] (which is not a case here, as discussed in section SIII.A of SM) and can be created experimentally by a careful convolution of many laser-field modes, as illustrated by its Fourier expansion in section SIII.B of SM. The application of our VHQCA to H atom when \( \omega = 0.06 \) is studied in detail in section 3, while in section 4 we set \( \omega = 0.222 \) (\( \lambda \approx 189 \text{ nm} \), i.e. single photon energy about 6.04 eV). In latter case \( F(t) \) in equations (4) has a few cycles during a single pulse, as shown in figure 1 (thin red line).

In order to obtain benchmarks for testing the numeric accuracy of our quantum algorithms which we derive in in section 2, 3 and 4, the system wave function is expanded in a finite truncated set of \( N \) bound hydrogenic eigenfunctions \( |\varphi_i\rangle \), where \( N = 2, 4, 8, \) or 16:

\[
\psi(r, t) = \sum_{i=1}^{N} c_i |\varphi_i\rangle
\]

where \( c_i \) is the amplitude of each \( |\varphi_i\rangle \). When replaced in equation (1), this expansion yields a finite set of coupled, time-dependent Ordinary Differential equations (ODEs) which approximate the Schrodinger equation.

The set of coupled ODEs is solved highly accurately using standard classical numerical methods with backward differentiation formula (Python scipy.integrate.ode function [52]). The absolute and relative tolerance at each step are set to \( 10^{-12} \) and \( 10^{-6} \) respectively to provide sufficient accuracy. The obtained time-dependent transition probabilities from 1s state for \( N = 2, 4, 8, 16 \) systems with unipolar HCP field \( (\omega = 0.06) \) are plotted in figure S1 of Supplemental Material, and for \( N = 4, 8, 16 \) systems with laser field \( \omega = 0.222 \) are plotted in figure S2. The benchmark transition probabilities at \( t = T = 200 \) are listed in section SII of SM. In figure 2 we plot the evolution of the transition probabilities in time for \( N = 16 \) system using laser field with (a) \( \omega = 0.06 \) and with (b) \( \omega = 0.222 \).

\[2.2. \text{VHQCA for time-dependent problems}\]

To simulate a system dynamics using variational algorithms, the system wavefunction \( \psi(r, t) \) can be approximated by a parameterized ansatz as a trial state \( \phi(\Theta(t)) \), where the time dependent parameter vector \( \Theta(t) \) has components \( \theta_i(t), i = 1, \ldots, L \), and \( L \) is the total number of parameters. The equation (1) then takes the form:

\[
\sum_i \frac{\partial |\phi(\Theta(t))\rangle}{\partial \theta_i} \theta_i + i[H, \phi(\Theta(t))]) \approx 0
\]

In the limit \( \phi \rightarrow \psi \), the equation (7) tends to Schrodinger equation. The algorithms for evolving the vector \( \Theta(t) \), convenient for computer processing, can be obtained using the Dirac-Frenkel [53, 54] or MLVP [36]. These variational principles are equivalent [20] when the components of \( \Theta(t) \) are complex numbers. However, all operators in quantum computing of a closed quantum system are unitary operators, with exception of measurement and reset operations. These can be represented by unitary matrices, preserving the inner product of two arbitrary states, and overall unitarity of the system. It requires that all variational parameters which represent real angles of the appropriate single qubit or two-qubits controlled rotation gates in quantum circuits.
are real numbers. The MLVP is derived assuming real variational parameters, and the solutions for derivatives in real time are always real. This makes MLVP our method of choice in implementations of the VHQCAs to the time-dependent problems in quantum computing.

In MLVP, the variation of real $\dot{q}$ yields the system of equations (shown in section SIV of SM), where the gradient of parameters can be calculated. Since the time derivative of the ansatz, $\dot{|\psi(t)|}$, is included in the time-dependent variational algorithm (equation S12 in SM), it could suffer a substantial deviation from the exact $\frac{\partial}{\partial t}|\psi(t)|$ if global phase is not included into consideration [20]. The improved equations for the time derivative of the vector $\theta(t)$ with extra global phase correction (GPC) terms take the form [20]:

$$\sum_j M_{ij} \dot{\theta}_j = V_i$$

where

$$M_{ij} = A^R_{ij} + \frac{\partial}{\partial \theta_i} \langle \phi(\theta(t)) | \frac{\partial}{\partial \theta_j} \langle \phi(\theta(t)) | \phi(\theta(t)) \rangle$$

$$V_i = C^I_i + \frac{\partial}{\partial \theta_i} \langle \phi(\theta(t)) | \phi(\theta(t)) \rangle \langle \phi(\theta(t)) | H | \phi(\theta(t)) \rangle$$

and $A^R_{ij}$ and $C^I_i$ are defined in section IV of SM.

The full derivation of equations (8) and (9) is provided in section SV of SM. Our calculations in section SVIII of SM show that algorithm equipped with the GPC produces significantly more accurate results than non-GPC version (equation S12 in SM) with the use of the same number of variational parameters and the same size of the time steps. This leads to more accurate calculations of the transition probabilities, at least in case of an atom in a laser field.

With $\theta(t)$ as input at time $t$, $M$ and $V$ are computed from quantum circuits, as explained later in section 2.5. The equations (8) are solved for $\theta$ using classical computing, by inversion of matrix $M$ with LU factorization using Python Numpy function numpy.linalg.inv [55]. Vector $\theta$ for the next time step is obtained via explicit marching methods with the knowledge of $\theta$, which enables the quantum computing of $M$ and $V$ at the new time. The whole process is sketched in figure 3, leading to the wave function at the targeted final time $T$.

Figure 2. The benchmark results for the transition dynamics of the 16-state $H$ model systems with laser pulse of (a) $\omega = 0.06$ and (b) $\omega = 0.222$. 

Projecting the eigenstates of the unperturbed Hamiltonian onto the $\phi(\theta(T))$, one obtains the S-matrix elements for transition to all states of the used truncated basis set starting from a chosen initial state of the system, defined by $\phi(\theta(t))$ at initial time $t = 0$. We also note that we calculate the transition amplitudes at times $0 < t < T$, while
the perturbation $P$ is on. In spirit of defining initial and final states of the system when the laser is off, the intermediate amplitudes and respective transition probabilities do not have a measurable physical meaning beyond being coefficients in equation (6), since the system does not have eigenstates while the time-dependent perturbation is on.

A common time-marching method for updating the variational parameters used in VHQCAs [19, 34, 35] is the explicit forward Euler method [56] which is denoted here as the First-Order Marching (FOM):

$$\theta_{t+\delta t} = \theta_t + \dot{\theta}_t \cdot \delta t + \mathcal{O}(\delta t^2)$$

where $\delta t$ is predefined fixed step size of the evolution algorithm.

To mitigate the need for a smaller step in our time marching, and reduce the number of steps needed to reach the final time $T$, we rather use the explicit forward Adams-Bashforth second order (AB2) scheme [57], based on the second-order Taylor series expansion, denoted here as the Second-Order Marching (SOM):

$$\theta_{t+\delta t} = \theta_t + \frac{3\dot{\theta}_t - \ddot{\theta}_t \cdot \delta t}{2} + \mathcal{O}(\delta t^3)$$

We find that the use of SOM increases the speed of marching allowing to reach the same accuracy as with FOM, using larger-size time-steps, i.e. with smaller overall number of steps. Thus the SOM saves the number of needed steps throughout the system evolution by about an order of magnitude, with proportional saving of the computing time. It is noteworthy that SOM produces the $\theta_{t+\delta t}$ using the historical evolution data $\dot{\theta}$ from only two previous steps.

2.3. Encoding of the Hamiltonian
The central issue in simulation of a quantum system using quantum computers is to encode the system into a form accessible by a quantum circuit. The occupations of atomic orbitals which form different fermionic configurations are mapped to the corresponding qubit configurations, and similarly the fermionic state operators are mapped to qubit state operators. To start the encoding, it is convenient to express the single electronic states in the Fock population basis [58]. For a system with 1 electron and $N$ atomic orbitals, there is a total of $N$ fermionic configurations. Each fermionic configuration can be defined as a vector $|f\rangle = |x_{N-1}, \ldots, x_0\rangle$, where $x_k \in \{0, 1\}$ representing the occupation of electron (0 for vacant and 1 for occupied) on the $k$th orbital defined by the basis function $|\varphi_k\rangle$, where orbital indexes $k$ are sorted in a descending order of the orbital energy. Hence, we can obtain the configuration set $\{ |f_0\rangle, \ldots, |f_{N-1}\rangle \}$, where each $|f_k\rangle$ is aligned in an ascending order of $k$,
indicating that the electron is present in the kth atomic orbital. Then the fermionic configuration set is ready to be mapped to qubit configuration set \( \{|q_0\}, \ldots, |q_{N-1}\rangle \) where \(|q_k\rangle\) is also sorted in an ascending order.

The fermionic Hamiltonian needs to be mapped to qubit Hamiltonian. By using the secondary quantization, one can obtain the single-electron Hamiltonian [59]:

\[
H = \sum_{i,j} h_{ij} a_i^\dagger a_j
\]

where \(h_{ij}\) are the one-electron integrals for the chosen basis set \(|\phi\rangle\) defined as:

\[
h_{ij} = \langle \varphi | H(r, t) | \varphi \rangle = \langle \varphi | H_0(r) + P(r, t) | \varphi \rangle.
\]

(a) and \(a_i\) are electron creation and annihilation operators, respectively, acting on fermionic states, defined as:

\[
a_k |x_k, x_{k-1}, \ldots, 0\rangle = (1 - x_k)(-1)^{\sum_{l=0}^{k-1} x_l} |x_k, x_{k-1}, \ldots, x_0, 1, \ldots\rangle
\]

(14a)

\[
a_k |x_k, x_{k-1}, \ldots, 0\rangle = x_k(-1)^{\sum_{l=0}^{k-1} x_l} |x_k, x_{k-1}, \ldots, x_0 - 1, \ldots\rangle
\]

(14b)

### 2.3.1. Unary encoding

Encoding methods such as JWE [37], parity encoding [60] and Bravyi-Kitaev encoding [61] are commonly used in simulation of many-body systems using quantum algorithms such as VQE [10, 17, 26, 62, 63], quantum simulation via Trotterization [31, 32], variational fast forwarding for quantum simulation [64] and McLachlan VHQCAs [34, 38]. The common feature of the listed methods is that the occupation of the kth atomic basis state is directly mapped to the state of the kth qubit, resulting in mapping of N atomic states to N qubits, known as the unary encoding method [30]. In the unary encoding, the kth qubit configuration \(|q_k\rangle\) is one of the computational basis of N qubits \(|q_k\rangle = |y_{N-1} = 0, \ldots, y_k = 1, \ldots, y_0 = 0\rangle\), where \(y_k \in \{0, 1\}\) is a basis state of an individual qubit. An example of encoding of a 4-state system using 4 qubits is shown in Table 2.

In this work, we apply the JWE as an example of unary encoding. According to this transformation, the operators \(a^\dagger\) and \(a\) are mapped to the qubit raising and lowering operators \(\sigma^+\) and \(\sigma\):

\[
a_k^\dagger = Z \otimes \cdots \otimes Z \otimes \sigma_k^+ \otimes I \otimes \cdots \otimes I
\]

(15a)

\[
a_k = Z \otimes \cdots \otimes Z \otimes \sigma_k \otimes I \otimes \cdots \otimes I
\]

(15b)

where

\[
\sigma^+ = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} = \frac{1}{2}(X - iY)
\]

(16a)

\[
\sigma = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} = \frac{1}{2}(X + iY)
\]

(16b)

I, X, Y, Z are Pauli matrices, and index \(k\) denotes the operation on the \(k\)th atomic state, encoded by the qubits. The qubit Hamiltonian obtained from the JWE using 4 qubits for the 4 mutually coupled states \((1s, 2p, 3s, 3d)\) of the hydrogen atom-laser system is shown in equation S24 of SM. The derivation for a general undetermined 4-state Hamiltonian encoded by JWE is provided in equation S25 of SM.

It is important to note that unary encoding, which is employed in this \(N\)-state system, operates within a \(2^N\)-dimensional Hilbert space formed by \(N\) qubits. Consequently, this encoding does not fully harness the quantum advantage it potentially offers. For instance, as illustrated in Table 2, the 4-qubit Hilbert space encompasses a total of 16 basis states forming the computational basis. However, only 4 of these basis states are utilized, leaving the remaining 12 computational basis states unused.

### Table 2. Examples of encoding 4-state system using JWE and QEE methods.

| Fermionic configuration \( |f\rangle = |x_1, x_2, x_3, x_4\rangle \) | JWE \(|q\rangle = |y_1, y_2, y_3, y_4\rangle \) | QEE \(|q\rangle = |y_1, y_4\rangle \) |
|---|---|---|
| 0001 | 0001 | 00 |
| 0010 | 0010 | 01 |
| 0100 | 0100 | 10 |
| 1000 | 1000 | 11 |
Regarding the scalability of unary encoding, it is worth mentioning that the number of Pauli terms scales as $O(N^4)$ with the number of qubits $N$ [62, 65, 66]. This scaling behavior provides insight into the computational resources required for unary encoding.

### 2.3.2. Compact encoding

To make advantage of all states in the computational basis and reduce the number of qubits to represent the ansatz, we utilize the compact, QEE method. With the compact mapping, a $N$-state system is encoded using $N_c = \log_2 N$ qubits. For example, for a 4-state system, only 2 qubits are needed to describe the system, as shown in table 2.

To obtain the qubit Hamiltonian for QEE of the hydrogen laser-atom system, one can start from the secondary quantized Hamiltonian in equation (12), and rewrite the excitation operators as [39]:

\[
a_i^+ a_j = |f_j\rangle \langle f_i|
\]

where the fermionic excitation operators $|f_j\rangle \langle f_i|$ enable the electron transition from state $|f_i\rangle$ to state $|f_j\rangle$: $(|f_i\rangle \langle f_j|)(|f_j\rangle) = |f_i\rangle$. Since the $i$th and $j$th fermionic configurations are mapped to corresponding qubit configurations [30, 40], the qubit Hamiltonian can be written in form:

\[
H = \sum_{i,j} h_{ij} |q_j\rangle \langle q_i|
\]

where

\[
|q_i\rangle = |y_{N-1}\rangle \ldots |y_0\rangle
\]

The qubit excitation operator $|q_i\rangle \langle q_j|$ can be further factorized in individual qubit as $\otimes \prod_{k=0}^{N-1} |Y_k\rangle \langle Y_k|$ where $k$ is the qubit index, and then replaced by Pauli operations to obtain a full qubit Hamiltonian [30, 40]:

\[
|0\rangle \langle 0| = \frac{1}{2} (I + Z), \quad |0\rangle \langle 1| = \frac{1}{2} (X + iY) \\
|1\rangle \langle 1| = \frac{1}{2} (I - Z), \quad |1\rangle \langle 0| = \frac{1}{2} (X - iY)
\]

The two-qubit Hamiltonian encoded by QEE for the same 4 mutually coupled states (1s, 2p, 3s, 3d) system is shown in equation S26 of SM. The derivation for a general 4-state Hamiltonian encoded by QEE is provided in equation S27 of SM.

Comparing with the JWE, the qubit Hamiltonian for the 4-state system by QEE requires only $\log_2 4 = 2$ qubits, reducing the dimension of the Hilbert space from 16 (JWE) to 4 (QEE). One can expect that for a larger size problem QEE will save quantum resources dramatically. For example, in the 1024-state system, the unary JWE requires a total of 1024 qubits, while QEE requires only $\log_2 1024 = 10$ qubits. It is noteworthy that QEE is also applicable to many-body systems to reduce the number of needed qubits. In a many-body system with $m$ electrons and $N$ spin-orbitals, there are $\binom{N}{m}$ possible electronic configurations. A unary encoding scheme would require $N$ qubits to simulate the system evolution, while with QEE one needs only $\left\lfloor \log_2 \left( \binom{N}{m} \right) \right\rfloor$ qubits [39]. For example, in case of $N = 1,000,000$ states and two electrons, 39 qubits would be enough to describe all $\sim 5 \times 10^{11}$ configurations.

### 2.4. Quantum variational ansatz

In McLachlan VHQCA, the quality of time-dependent simulation is tied to the ability of the variational ansatz to correctly describe the many-state time-evolved wave function, which raises the challenge for constructing a sufficiently expressible and fully entangled ansatz [67] when using either JWE or QEE. In the quantum computing, the ansatz is prepared with a set of consecutive quantum gates to approximate the wavefunction. In this work, the circuit of ansatz $|\phi(\theta(t))\rangle$ and the circuit of the derivative of ansatz $\frac{\partial}{\partial \theta} |\phi(\theta(t))\rangle$ will be used as modules to construct the Hadamard test circuit at figure 6 to evaluate the values of equations (9), which will be introduced in section 2.5. The general single qubit parameterized gates $R_p(\theta_k)$ are defined as single qubit rotations by an angle $\theta_k$ about $p$ axis at the Bloch sphere, defined by a Pauli operator $p$ of a set $\{X, Y, Z\}$. The two-qubit parameterized gates $CR_p(\theta_k)$ are defined as controlled rotations applying a rotation $R_p(\theta_k)$ on a target qubit upon the state of the control qubit. Thus,

\[
R_p(\theta_k) = e^{-i\theta_k p/2}
\]

\[
CR_p(\theta_k) = |0\rangle \langle 0| \otimes I + |1\rangle \langle 1| \otimes R_p(\theta_k)
\]
where $N$ freedom of variations for each state. For a general parameterized gate with their derivative forms. For example, de 2.4.1. Ansatz for unary encoding

controlled rotation gate is treated as a linear combination of two circuits. The amplitudes for each qubit basis state, also essential in enabling GPC to increase accuracy of the results.

Therefore, the derivative of $\theta_k$ applied to ansatz can be obtained by replacing the corresponding parameterized gate with their derivative forms. For example, defining ansatz with three rotations applied to the initial qubit state $|0\rangle$, $\phi(\theta) = R_X(\theta_1)R_Y(\theta_2)R_Z(\theta_3)|0\rangle$, the derivative of ansatz over $\theta_2$ can be written as:

$$
\frac{\partial \phi(\theta)}{\partial \theta_2} = R_Z(\theta_3)\frac{\partial R_Y(\theta_2)}{\partial \theta_2}R_Z(\theta_3)|0\rangle = -\frac{i}{2} R_Z(\theta_3)XR_Z(\theta_3)R_Z(\theta_3)|0\rangle
$$

It is noteworthy that the derivative of a $CR_p(\theta_k)$ over $\theta_k$ is not a unitary matrix due to the presence of $0$’s along the main diagonal. Thus, to apply the derivatives in a quantum circuit, one needs to decompose them to a linear combination of unitary operators. For example, the derivative of $CR_X$ is expressed as

$$
\frac{\partial CR_X(\theta_k)}{\partial \theta_k} = -\frac{i}{2}(U \otimes (X \cdot CR_X(\theta_k))) + \frac{i}{2}(Z \otimes (X \cdot CR_X(\theta_k))).
$$

Hence, the derivative of ansatz over the parameter of a controlled rotation gate is treated as a linear combination of two circuits.

2.4.1. Ansatz for unary encoding

We construct the variational ansatz for unary encoding (JWE in this work), by an iterative layered structure, using the parameterized single-qubit and two-qubits controlled rotations around $X$ and $Z$-axis, as well as CNOT and $X$ gates. The circuit for a general $N$-state ansatz is shown in figure 4, which has symbolic form shown in equation (24). The combination of $R_X$ and $R_Z$ gates at each qubit ensures freedom of variation in both phases and amplitudes for each qubit basis state, also essential in enabling GPC to increase accuracy of the results.

Thus the formula for the ansatz in figure 4 has the form:

$$
|\phi(\theta_1, \ldots, \theta_{2N-2})\rangle = c_0 e^{-i \sum_{k=1}^{N-1} \theta_k} \cos \left( \frac{\theta_{N-1}}{2} \right) |q_0\rangle + \sum_{k=1}^{N-1} c_k e^{i \sum_{j=1}^{N-2-k} \theta_j} \prod_{j=N-k}^{N-1} \sin \left( \frac{\theta_j}{2} \right) \cos \left( \frac{\theta_{N-1-j}}{2} \right) |q_k\rangle
$$

where $N > 2$, $\theta_0 = 0$, $c_k = (-1)^{\frac{k}{2}}$ for even $k$, and $c_k = (-1)^{\frac{k+1}{2}}i$ for odd $k$. From equation (24), one can see that the $R_X$ and $CR_X$ rotations in the ansatz contribute to amplitude, while the $R_Z$ rotations update phase of each basis state. The $N$-qubits problem representing $N$ atomic states requires a total of $2(N - 1)$ parameters and $(3N - 2)$ gates, specifically $(N - 2)$ Control-$R_X$ gates, $(N - 1)$ CNOT gates, $(N - 1)$ $R_Z$ gates, one $R_X$ gate and one $X$ gate, as listed in table 3.

2.4.2. Ansatz for compact encoding

The QEE, as a compact encoding method, uses the computational basis in full, utilizing a streamlined hardware-efficient variational ansatz to ensure the coverage of the full Hilbert space [29]. For $N$ atomic states represented by $log_2 N$ qubits, the same number of parameters as in corresponding unary cases are used to ensure the same freedom of variations for each state. For a general $N$-state case, there are $2(N - 1)$ single parameterized rotations and $2(N - 1 - \log_2 N)$ CNOT gates [29]. Similarly, the combination of $R_Y$ and $R_Z$ gates provides an approximation for each basis state phase and amplitude, respectively. The circuits for 2 and 3 qubits are shown in figure 5. The symbolic form of the 2-qubit ansatz takes the form:
The symbolic forms of ansatz for more than 2 qubits become too messy to be written here. The JWE and QEE for the N-state problem have similar total number of parameterized gates in the ansatz computation. However, nearly a half of parameterized gates in JWE ansatz are two-qubit $\text{CRX}$ gates, while in the QEE ansatz all parameterized rotation gates are the single-qubit operations. It is noteworthy that the controlled parameterized rotation $\text{CRX}$ in the unary encoding cannot directly be executed by the quantum computers. Instead, it has to be decomposed to a set of one and two-qubit gates which are considered as elementary basis gate and can be operated in the quantum computers. The decomposition of $\text{CRX}$ gates generates a much deeper circuits than single-qubit $\text{RY}$ gates in QEE ansatz. An example of the gate decomposition for the real IBM device backend ibmq_jakarta is shown in figure S4 of the SM. After decomposition, the depth of a $\text{CRX}$ circuit is more than twice as big as that of a decomposed $\text{RY}$ circuit. Hence the total number of 2-qubit gates and single qubits gates actually executed on quantum computers is significantly smaller with the QEE ansatz than with JWE ansatz.

Moreover, using QEE enables quantum devices to map exponentially larger systems compared to the approach using JWE. This reduction in the number of qubits and quantum operations is particularly significant for NISQ implementations as it alleviates the demand for larger-scale quantum computers. Large-scale quantum computers, with their requirement for excessively long T1 times and high-fidelity operations, are more susceptible to undesirable external disturbances and signal path couplings, commonly known as “crosstalk” [68, 69]. Saving both width (number of qubits) and depth of quantum circuits leads to the smaller noise effects. However, the downside of the QEE is its complexity to generalize ansatz in a symbolic form for large N, which downgrades the simulation speed.

### 2.5. Hadamard test circuits

To obtain expectation values of all terms in equations (9), we use the Hadamard test with the circuits shown in figure 6, where only an ancilla qubit is measured. The Hadamard test shown here describes a general circuit for measurement of the real part of expectation value of an operator $U$, $\mathcal{R}(\phi(\mathbf{\theta}(t)))|U|\phi(\mathbf{\theta}(t))$. The expectation

![Figure 5. Variational ansatz for QEE with 2(a) and 3(b) qubits.](image)

### Table 3. Comparison of two encoding methods for a N-state system.

| Encoding method | JWE $\log_2 N$ |
|----------------|----------------|
| Number of qubits | $N$ |
| Total gates | $3N - 2$ |
| Total variational parameters | $2(N - 1)$ |
| Number of single parameterized gates | $N$ |
| Number of controlled parameterized gates | $N - 2$ |
| Number of CNOT gates | $N - 1$ |

\[
|\phi(\mathbf{\theta})| = e^{i\left(-\theta_1 - \theta_2 - \theta_3\right)} \cos\left(\frac{\theta_1}{2}\right) \cos\left(\frac{\theta_2 + \theta_3}{2}\right)|00\rangle + e^{i\left(-\theta_1 + \theta_2 + \theta_3\right)} \cos\left(\frac{\theta_1}{2}\right) \sin\left(\frac{\theta_2 + \theta_3}{2}\right)|01\rangle + e^{i\left(\theta_1 + \theta_2 - \theta_3\right)} \sin\left(\frac{\theta_1}{2}\right) \cos\left(\frac{\theta_2 - \theta_3}{2}\right)|10\rangle + e^{i\left(\theta_1 - \theta_2 + \theta_3\right)} \sin\left(\frac{\theta_1}{2}\right) \sin\left(\frac{\theta_2 - \theta_3}{2}\right)|11\rangle
\]

(25)
value is calculated as the difference between probabilities measuring state |0⟩ and |1⟩. Unitary operations \( U_0, U_A, U_h \) and \( U_B \) in figure 6 are defined by various measured quantities, listed in table 4. \( U_0 \) represents the unitary operations for preparing an ansatz. \( U_A \) and \( U_B \) are the circuits for calculations of various terms in \( M \) and \( V \). \( U_h \) can be replaced by Pauli gate in various qubit Hamiltonian terms, while the matrix elements \( h_{ij} \) of \( H \) are multiplied with measured results for the final expectation values. It is noteworthy that a derivative of ansatz gives an imaginary coefficient \(-\frac{i}{2}\), as shown in equations (22), which is extracted to be post-processed with measurement results. Hence the evaluation of \( \frac{\partial \langle \phi(\theta(t)) \rangle}{\partial \theta} \) and \( C_f \) by the circuits in figure 6 is equivalent to the measurement of the real parts of \(-\frac{i}{2} \frac{\partial \langle \phi(\theta(t)) \rangle}{\partial \theta} \) and \(-\frac{1}{2} \frac{\partial \langle \phi(\theta(t)) \rangle}{\partial \theta} H \langle \phi(\theta(t)) \rangle \).

### 3. Results

#### 3.1. Unipolar HCP field with \( \omega = 0.06 \)

The evolution from \( t = 0 \) to \( t = 200 \) a.u. of a hydrogen atom, modeled by a finite number of bound states and irradiated by a unipolar HCP involves 2000 to 200,000 marching steps, depending on the choice of a step size \((\Delta t = 10^{-1} - 10^{-3})\). To obtain the results quickly and efficiently, the symbolic simulation is applied to all tests in this section, which uses the symbolic expressions to numerically simulate the results of quantum circuits, instead of doing common gate-based simulation. Ansatz is a function of \( t \) of doing common gate-based simulation. The symbolic simulation is carried out using Python Sympy and Numpy packages. The symbolic simulation with JWE can be conveniently done for arbitrary \( N \) having the general expression for ansatz (equation (24)). However, in the QEE approach the symbolic calculation becomes difficult when \( N_q > 3 \) since the expressions for ansatz become formidable.

In the experiments in this section, only ground state is fully populated at the beginning. The GPC (equation (8)), SOM (equation (11)) and the time step size \( \Delta t = 10^{-3} \) are applied in all computations to achieve the best accuracy and the optimal results are shown in this section for discussion. For comparison, two sets of tests are conducted to investigate the performance of algorithms with different techniques: (a) without GPC (equation S12), with SOM and \( \Delta t = 10^{-4} - 10^{-5} \), (b) with GPC, FOM (equation (10)) and \( \Delta t = 10^{-4} - 10^{-5} \). The results of these two tests are listed in section S25 of SM. All the tests are done with both JWE and QEE to provide a fair comparison between two encoding methods. Note that the common quantum gate-based simulator is not used here due to a high demand of computation power and time for simulation of the system evolution. However, we partially provided the simulation results with QEE from gate-based simulator, Pennylane [70], in section S6 of SM to prove that the obtained transition probabilities from the symbolic simulation are at the same level of accuracy as the gate-based simulation as they are mathematically equivalent.

The final transition probabilities \( P(T) \) are recorded and compared with the benchmark results \( P_{\text{ref}} \) (listed in table S2 of SM) for the models with various \( N \). The relative deviations of \( P(T) \) from the benchmark values \( P_{\text{ref}} \)
Table 5. The Relative Deviations (RD, in %) of the final transition probabilities from symbolic simulation comparing to the benchmark for the 2, 4, 8-state systems using QEE and 16-state system using JWE with SOM, GPC, $\Delta t = 10^{-3}$ and the laser field of $\omega = 0.222$.

|        | QEE                  | JWE                  |
|--------|----------------------|----------------------|
| $N$    | Orbitals | RD     | $N$    | Orbitals | RD     |
| 2 states | 2p       | $2.61e-2$ | 16 states | 6s  | $1.93e-1$ |
| 1s      | $1.00e-5$ | 4s      | $8.90e-2$ |
| 3d      | $2.49e-2$ | 5d      | $2.07e-1$ |
| 3s      | $-4.40e-4$ | 5f      | $-2.07e-1$ |
| 2p      | $-8.33e-3$ | 2s      | $3.31e-1$ |
| 1s      | $-2.60e-4$ | 4f      | $6.34e-3$ |
| 4p      | $5.27e-2$  | 4d      | $-2.04e-1$ |
| 4s      | $4.47e-1$  | 3d      | $-8.42e-2$ |
| 3d      | $7.56e-3$  | 3s      | $-3.42e-2$ |
| 3p      | $-2.31e-2$ | 3p      | $-3.91e-2$ |
| 3s      | $4.06e-3$  | 3s      | $-3.42e-2$ |
| 2p      | $-9.43e-3$ | 2p      | $-3.44e-2$ |
| 2s      | $-2.32e-2$ | 2s      | $-5.37e-2$ |
| 1s      | $1.46e-2$  | 1s      | $4.83e-2$  |

are also calculated for various $N$. We define the absolute value of relative deviation at 1% as the accuracy threshold, below which the results are considered accurate enough. The results with optimal conditions are presented in table 5. The QEE is applied for the hydrogen model with $N = 2, 4, 8$ hydrogen eigenstates, with 1, 2 and 3 qubits, respectively. And the Unary encoding is applied for $N = 16$ system which requires 16 qubits in the circuits. Note that if the number of states is not a power of 2, one can still do the QEE by adding null states to get $N = 2^N$. All null states have no interaction with any other state and are initialized to the zero population.

With the step size of $10^{-3}$ (0.024 a.s.), the accepted accuracy threshold is obtained for all $N$ cases. Comparing to the results with larger time step size shown in table SV (JWE) and SVIII (QEE) in Supplemental Material, for 2 and 4-state cases, the accuracy is achieved with step size $\Delta t = 10^{-1}$. When lowering the step size to $10^{-2}$, the absolute relative deviation decreases up to one magnitude. The results with $\Delta t = 10^{-3}$ show large relative deviations from the benchmark in 8-state cases, which are greatly improved with $\Delta t = 10^{-3}$, reaching the acceptable accuracy with $\Delta t = 10^{-3}$.

The results obtained by varying the choice of SOM or FOM, and with or without GPC are presented in figure S6 (JWE) and figure S7 (QEE) of SM, to quantify the improvements GPC and SOM brought to the results. The data are listed in section SVIII of SM. The substantial relative deviations is found in non-GPC cases, indicating the necessity of GPC for accurate results in implementation of the McLachlan in VHQCAs. Also the results show that using SOM allows one magnitude larger step size to reach accuracy threshold than using FOM, which saves the computation time by one order of magnitude. More detailed discussion and analysis can be found in section SVIII.

The results of using JWE in section SVIII.A show a generally similar accuracy as QEE results (section SVIII. B). Interestingly, with $\Delta t = 10^{-3}$ in the 4 and 8-state systems, the relative deviations of QEE results reduce up to one order of magnitudes in comparison to the ones of JWE results. All of above indicates the advantages of using SOM and GPC with QEE, by bringing a logarithmic reduction in the number of required qubits, hence less computational resource and time, while maintain the same level of precision (in some case even better precision).

3.2. Laser field with $\omega = 0.222$

Here we test the system interacting with short laser pulse with high frequency of $\omega = 0.222$. The laser electric field in this case has a few cycles, causing different transition probabilities than unipolar HCP, as shown in figure S2 of SM. Three cases are tested here using symbolic simulations: 4, 8-state systems using QEE and 16-state system using JWE. The relative deviations of the results from the benchmark are presented in table 6.
NISQ era
Since quantum computing version of McLachlan variational algorithm is initially proposed as a solution for 4. Effects of quantum noise
noise simulation on a gate-based quantum simulator. To investigate the noise resistance of the algorithm under benchmarks well below the threshold of 1%. This is also a case for the 4-states system even with the time step size are similar for the two types of the strong laser which is not shown here. We note that the conclusions on the accuracy of the calculated results with respect to the method to reduce the noise accumulation when simulating a strongly time-perturbed systems with many states is missing. The evaluation of the algorithm performance due to the sampling errors and with inclusion of a real hardware noise model are carried out and discussed in this section. In the tests of the noise effects, quantum circuits are constructed with IBM Quantum Information Science Kit (QISKit, version 0.30.0) with the quantum noise modelled from the properties of the IBM Q quantum device backend ‘ibmq_jakarta’. This device noise model is constructed from the calibration data with depolarizing errors at both single and two-qubit gates, thermal relaxation errors for simulating decoherence at all gates, and single-qubit readout errors on all individual measurements. The details of calibration data are provided in the section SX of SM. While advancements in quantum technology are expected to reduce quantum noise, it is important to note that sampling errors remain intrinsic and inevitable, even with improved hardware. The collapse of the wavefunction due to quantum measurements requires a statistical approach by preparing and measuring circuits in repetitions (known as shots), which cause the sampling errors. The sampling errors can be reduced by increasing the number of shots until a desired statistical accuracy is achieved, but at the cost of using more quantum resources and longer time. While several studies have explored the application of machine learning techniques to mitigate the impact of sampling errors [72–74], addressing this aspect is beyond the scope of our current study. The system dynamics with only sampling errors involved are also tested here as the reference. All quantum circuits in this section are measured with 50,000 shots.

For demonstration, we chose 4-state system utilizing QEE (2 qubits), with SOM and GPC included in all tests of this section. The step size is chosen at $\Delta t = 10^{-1}$ due to a high demand of computation power and time for noise simulation on a gate-based quantum simulator. To investigate the noise resistance of the algorithm under various representations, we applied both Hamiltonian in Schrodinger Representation (SR) (equation (18)) and in Interaction Representation (IR) [75]. In IR we assume a new $\psi(r, t) = e^{-ik_{\rho}r(t)}\psi(r, t)$, which unitarily transforms matrix elements $h_{ij}$ of the Hamiltonian (equation (18)) into:

\begin{table}[h]
\centering
\caption{The Relative Deviations (RD, in %) of the final transition probabilities from symbolic simulation comparing to the benchmark for the 4, 8-state systems using QEE and the 16-state system using JWE with SOM, GPC, $\Delta t = 10^{-3}$ and the laser field of $\omega = 0.222$.}
\begin{tabular}{cccc}
| N | Orbits | RD | N | Orbits | RD |
|---|---|---|---|---|---|
| 4 states | 3d | 3.51e−2 | 16 states | 6s | 4.99e−1 |
| | 3s | 3.19e−1 | | 5g | −2.36e−2 |
| | 2p | −1.21e−1 | | 5d | −1.88e−1 |
| | 1s | −2.60e−2 | | 5p | −3.99e−3 |
| 8 states | 4p | −1.83e−2 | | 4d | −2.57e−2 |
| | 4s | −2.64e−2 | | 4p | 7.87e−3 |
| | 3d | −1.80e−2 | | 4s | 2.15e−2 |
| | 3p | −1.83e−2 | | 3d | −3.22e−2 |
| | 3s | −1.08e−2 | | 3p | 1.35e−3 |
| | 2p | −1.90e−4 | | 3s | 4.30e−3 |
| | 2s | 2.90e−4 | | 2p | −2.02e−2 |
| | 1s | 8.86e−2 | | 2s | 4.00e−5 |
| | | | | 1s | 8.74e−2 |
\end{tabular}
\end{table}

All results with the optimal setting (SOM, GPC and $\Delta t = 10^{-3}$) show relative deviations from the benchmarks well below the threshold of 1%. This is also a case for the 4-states system even with $\Delta t = 10^{-2}$, which is not shown here. We note that the conclusions on the accuracy of the calculated results with respect to the time step size are similar for the two types of the strong laser field in sections 3.1 and 3.2.

4. Effects of quantum noise

Since quantum computing version of McLachlan variational algorithm is initially proposed as a solution for NISQ era [19], it is also very important to investigate the algorithm performance in presence of quantum noise. For example, in [19] Li et al explored the noise performance and potential error mitigation techniques of McLachlan VHQCA with an example of simulating a quantum Ising model of 3 spins. But the noise effects and the method to reduce the noise accumulation when simulating a strongly time-perturbed systems with many states is missing. The evaluation of the algorithm performance due to the sampling errors and with inclusion of a real hardware noise model are carried out and discussed in this section. In the tests of the noise effects, quantum circuits are constructed with IBM Quantum Information Science Kit (QISKit, version 0.30.0) [71] with the quantum noise modelled from the properties of the IBM Q quantum device backend ‘ibmq_jakarta’. This device noise model is constructed from the calibration data with depolarizing errors at both single and two-qubit gates, thermal relaxation errors for simulating decoherence at all gates, and single-qubit readout errors on all individual measurements. The details of calibration data are provided in the section SX of SM. While advancements in quantum technology are expected to reduce quantum noise, it is important to note that sampling errors remain intrinsic and inevitable, even with improved hardware. The collapse of the wavefunction due to quantum measurements requires a statistical approach by preparing and measuring circuits in repetitions (known as shots), which cause the sampling errors. The sampling errors can be reduced by increasing the number of shots until a desired statistical accuracy is achieved, but at the cost of using more quantum resources and longer time. While several studies have explored the application of machine learning techniques to mitigate the impact of sampling errors [72–74], addressing this aspect is beyond the scope of our current study. The system dynamics with only sampling errors involved are also tested here as the reference. All quantum circuits in this section are measured with 50,000 shots.

For demonstration, we chose 4-state system utilizing QEE (2 qubits), with SOM and GPC included in all tests of this section. The step size is chosen at $\Delta t = 10^{-1}$ due to a high demand of computation power and time for noise simulation on a gate-based quantum simulator. To investigate the noise resistance of the algorithm under various representations, we applied both Hamiltonian in Schrodinger Representation (SR) (equation (18)) and in Interaction Representation (IR) [75]. In IR we assume a new $\psi(r, t) = e^{-ik_{\rho}r(t)}\psi(r, t)$, which unitarily transforms matrix elements $h_{ij}$ of the Hamiltonian (equation (18)) into:
In the noise-free simulations, Schrodinger and interaction representations yield the same results. The algorithm is first tested without laser field, where all 4-state initial \( \rho(0) \) amplitudes are set to equal values \( = 0.5 \). The results are presented in section SXI of SM. Since the perturbation \( P(r, t) = 0 \), the variational parameters and the transition probabilities should stay constant with time if without any noise and error. In the noise simulation, when using SR Hamiltonian, serious errors accumulate throughout the time even in absence of any external time-dependent perturbation (figure S8). However, the results with the IR Hamiltonian show no error accumulation throughout the evolution (figure S9), indicating the use of Hamiltonian in IR is a necessity in the NISQ era to significantly improve the noise-resistance for quantum computing applications presented in this work.

The impact of the quantum noise and sampling to the transition dynamics of a hydrogen atom modeled with only 4 states with the short laser pulse perturbation (the same model studied in section 3.2 with \( \omega = 0.222 \)) is also evaluated. The noise-free symbolic simulation results in section 3.2 are used as the reference to calculate the deviation of the final state probabilities caused by noise. The deviations of the transition probabilities in presence of a) sampling error only and b) with both device noise and sampling error are shown in figures 7 and 8 (SR and IR respectively), for times between \( t = 0 \) and \( t = 200 \). The accumulation of the noise effects appears mainly while the laser field is strong (for \( t \) between 20 and 80). With SR Hamiltonian, sampling errors are in acceptable range (figure 7(a), however the device noise errors accumulate even when the laser field is off, increasing almost linearly with time (figure 7(b)). When IR Hamiltonian is used (figure 8), the state probabilities, and therefore deviations stay constant as expected after \( t > 100 \). In this case the sampling error does not deteriorate the accuracy of the final results more than a few percent (figure 8(a)). The device noise contributes a few times more to the errors (figure 8(b)). These results are in accord with the conclusions of section SXI that the IR Hamiltonian yields a noise resistance when the time-dependent perturbation is off. This brings the presented algorithms a
step closer to the practical implementations for the time dependent quantum systems in the NISQ devices with improving noise characteristics.

5. Conclusions

We propose hybrid, quantum–classical algorithm for simulation of evolution and multi-state transition dynamics of a single electron atom, subject to a strong, attosecond time-dependent perturbation. This problem is still formidable to apply to a multi-electron system at a quantum computer. We focus to the important properties, advantages and difficulties when computing dynamics of a fully entangled, hydrogen atom model of 16 states in a strong, attosecond laser field, utilizing McLachlan variational principle.

One challenge for the algorithm is to construct a sufficiently expressible variational ansatz, capable to describe the fast time evolution and transition dynamics fully and accurately for a system wave function, with a need for repeated calculations at many time steps during the strong, time dependent perturbation of the Hamiltonian (up to 200,000 to reach accuracy < 1% for all 16 states). Since McLachlan VHQCA is dependent on the time derivatives of the ansatz, the global phase correction must be taken into account for an accurate application of the algorithm. The second-order time marching for updating the variational parameters reduces needed number of steps by an order of magnitude, when compared with Euler first-order marching. We developed ansatz with both unary (Jordan-Wigner) and quantum efficient encoding (QEE) to compare their advantages and shortcomings. Both types of ansatz were efficient in reaching highly accurate wave function under the strong and short laser pulse perturbation. With unary encoding we were able to provide simple quantum circuits and analytical formula for construction a general N-state ansatz, using N qubits. QEE simulate the dynamic evolution with significantly lessen number of qubits, \( \log_2 N \), and with reduced quantum depth. The latter is achieved by replacing \( N - 2 \) two-qubit control-rotation gates with \( N - 2 \) single-qubit rotation gates, of importance for reducing the noise effects. However, when number of states increases, the QEE ansatz becomes
difficult for simulation, and the requirement of extremely low quantum noise for the hardware might be beyond the reach of the current NISQ-era quantum computers.

We also estimate the algorithm response to a quantum noise, modelled by a real hardware noise of ‘ibmq_jakarta’, as well as to the sampling errors. Accumulation of the errors is reduced several times during the laser-field pulse when using interaction representation rather than Schrodinger representation of the Hamiltonian (in hydrogenic basis). No error accumulation is present with IR when the laser interaction was off.

We systematically carried out quantification of the accuracy of our results by comparison with benchmarks, obtained by solving time-dependent Schrodinger equation with classical ODE methods. The error bound of the resulting transition probabilities of all excited states is strictly set to less than 1% for the end of the evolution (after the time-dependent perturbation is off) as a condition for acceptance of results. This made the proposed algorithm a promising method for computing the transition dynamics in a quantum system subject to the strong and short time dependent perturbations.

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The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request. All authors declare that they have no conflicts of interest.

Data availability statement

The data cannot be made publicly available upon publication because they are not available in a format that is sufficiently accessible or reusable by other researchers. The data that support the findings of this study are available upon reasonable request from the authors.

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