Quantum computation of molecular response properties

Xiaoxia Cai,¹ Wei-Hai Fang¹, Heng Fan,² and Zhendong Li^{1,*}

¹Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, China

²Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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Accurately predicting the response properties of molecules, such as dynamic polarizability and hyperpolarizability, using quantum mechanics has been a long-standing challenge with widespread applications in material and drug design. Classical simulation techniques in quantum chemistry are hampered by the exponential growth of the many-electron Hilbert space as the system size increases. In this work, we propose an algorithm for computing linear and nonlinear molecular response properties on quantum computers by first reformulating the target property into a symmetric expression more suitable for quantum computation via introducing a set of auxiliary quantum states, and then determining these auxiliary states via solving the corresponding linear systems of equations on quantum computers. On the one hand, we prove that when using the quantum linear system algorithm [Harrow *et al.*, *Phys. Rev. Lett.* **103**, 150502 (2009)] as a subroutine, the proposed algorithm scales only polynomially in the system size instead of the dimension of the exponentially large Hilbert space, and hence it achieves an exponential speedup over existing classical algorithms. On the other hand, we introduce a variational hybrid quantum-classical variant of the proposed algorithm that is more practical for near-term quantum devices.

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I. INTRODUCTION

How molecules respond to the action of external fields determines the properties of materials. For weak external fields, the response is fully characterized by the linear and nonlinear response functions [1,2], such as the polarizability tensor $\alpha_{ij}(\omega)$ and hyperpolarizability $\beta_{ijk}(\omega_1, \omega_2)$ ($i, j, k \in \{x, y, z\}$). The dynamic polarizability $\alpha_{ij}(\omega)$ describes how the dipole moment of a molecule responds to an oscillating electric field to leading order, and it can be linked to the photoabsorption cross section, while the first-order hyperpolarizability describes nonlinear response processes such as second-harmonic generation in nonlinear optical materials. In addition, these response functions are also the key to understanding intermolecular interactions. Notably, the van der Waals C_6 coefficients, which are of paramount importance in quantifying the dispersion interaction between drug molecules and proteins in drug design, can be computed from dynamic polarizabilities at imaginary frequencies via the Casimir-Polder integral [3].

Developing reliable quantum-mechanical methods for accurately predicting molecular response properties has been one of the major challenges in the field of quantum chemistry

[2,4,5]. The full configuration interaction (FCI) [6–8], also known as the exact diagonalization method, represents the most accurate method within a molecular orbital basis set; however, it is limited to small molecular systems due to the exponential growth of the many-electron Hilbert space as the system size increases. Over the past few decades, a plethora of approximate methods along with efficient algorithms have been developed [4,5]. Unfortunately, the approximations adopted in these methods to describe efficiently the correlation among electrons, such as the mean-field approximation [6] or approximate exchange-correlation functionals in density functional theory [9], can sometimes fail miserably. In particular, strong electron correlation [10], which is the basis for many fascinating phenomena in materials (e.g., high-temperature superconductivity), cannot be accurately accounted for by these approximate methods. A satisfactory classical simulation method for predicting molecular response properties that works in all electron correlation regimes is still lacking.

Initially advocated by Feynman [11], quantum computation shows great promise for solving interacting fermion problems in physics and chemistry [12–19]. The quantum phase estimation (QPE) algorithm [20] was applied to obtain the ground-state energies of molecules with an exponential speedup over the classical FCI [21]. It also allows us to compute molecular static properties via energy derivatives [22,23]. While QPE has only been realized for two-electron systems [24–27] due to the requirement of a long circuit depth, the variational quantum eigensolver (VQE) [28,29] is more suitable for noisy intermediate-scale quantum (NISQ) [30] devices. Unlike QPE, its advantage over classical simulation

*zhendongli@bnu.edu.cn

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techniques in quantum chemistry is still an open question and is being actively explored. Nevertheless, VQE has been experimentally demonstrated on various platforms for small molecules, such as H_2 , HeH^+ , LiH , and BeH_2 [27,28,31–33]. In view of such progress in the ground-state problem, it is a natural question to ask whether computing molecular response properties, as the next logical step after computing the ground state, will also benefit from quantum computation.

In this work, we propose an algorithm for computing molecular response properties on quantum computers. While dynamical properties can alternatively be obtained by Fourier transform of the corresponding correlation functions in the time domain [16,34,35] determined from real-time Hamiltonian simulations, analogous to the classical computation side [2,4,5], it is highly desirable to have a quantum algorithm for computing a target response property such as $\alpha_{ij}(\omega)$ or $\beta_{ijk}(\omega_1, \omega_2)$ at given frequencies directly. This is because in many molecular applications [2,4] only a small range of frequencies is of interest, including the simulations of (hyper)polarizabilities at specific frequencies of applied electromagnetic fields [8,36], absorption spectra in a visible/ultraviolet/X-ray region of interest [5], and multidimensional spectroscopies for studying couplings between selected modes [37]. By reformulating the target property into a symmetric expression with the help of a set of auxiliary quantum states, we convert the most demanding part of the computations into linear systems of equations for determining these states, which can be solved on quantum computers using quantum algorithms for linear systems of equations [38–42] or variational hybrid quantum-classical algorithms [43,44]. Depending on the subroutine employed for determining auxiliary states, the resulting variant of the proposed algorithm can be considered as the analog of QPE or VQE for molecular response properties. While the latter variational hybrid quantum-classical variant is more practical for near-term quantum devices, we prove that in combination with the quantum linear system algorithm invented by Harrow, Hassidim, and Lloyd (HHL) [38], the runtime complexity of the quantum variant of our algorithm scales polynomially in the molecular system size, instead of the dimension of the exponentially large many-electron Hilbert space. Thus, an exponential speedup can be achieved compared with the classical FCI-based approach [7,8], which established a firm foundation for future applications of quantum computation in predicting molecular response properties.

II. THEORY

For concreteness, we consider the calculation of the polarizability $\alpha_{zz}(\omega)$ for a molecule under a monochromatic electric field with optical frequency ω in the z -direction. The static polarizability will be obtained as a special case in which $\omega = 0$. Extensions to off-diagonal components of the polarizability tensor as well as nonlinear response properties are straightforward and will be discussed later.

Suppose initially without external fields a molecule with N electrons is in the ground state $|\Psi_0\rangle$ of the second-quantized electronic Hamiltonian $\hat{H}_0$, expressed in an orthonormal molecular spin-orbital basis $\{\psi_p\}_{p=1}^K$ (K is proportional to the

system size N) as

$$\hat{H}_0 = \sum_{p,q=1}^K h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{p,q,r,s=1}^K h_{pqrs} a_p^\dagger a_q^\dagger a_s a_r, \quad (1)$$

where $a_p^{(\dagger)}$ represents the fermionic annihilation (creation) operator, and h_{pq} (h_{pqrs}) represent the one-electron (two-electron) integrals. The dynamic electric field in the dipole approximation is associated with the perturbation operator

$$\hat{z} = \sum_{p,q=1}^K z_{pq} a_p^\dagger a_q, \quad (2)$$

where $z_{pq} \triangleq \langle \psi_p | z | \psi_q \rangle$ represent the dipole-moment integrals. Using the time-dependent perturbation theory, the frequency-dependent polarizability $\alpha_{zz}(\omega)$ can be expressed in a sum-over-state (SOS) form [1,2]

$$\alpha_{zz}(\omega) = \sum_{n>0} \left[\frac{\langle \Psi_0 | \hat{z} | \Psi_n \rangle \langle \Psi_n | \hat{z} | \Psi_0 \rangle}{\omega_{n0} - (\omega + i\gamma)} + \frac{\langle \Psi_0 | \hat{z} | \Psi_n \rangle \langle \Psi_n | \hat{z} | \Psi_0 \rangle}{\omega_{n0} + (\omega + i\gamma)} \right], \quad (3)$$

with $\gamma > 0$ being a phenomenological damping parameter, which is physically associated with the inverse lifetime of excited states. Computing $\alpha_{zz}(\omega)$ allows us to access important information about molecules, such as the transition dipole moments $\langle \Psi_0 | \hat{z} | \Psi_n \rangle$ between the ground state $|\Psi_0\rangle$ and the n th excited state $|\Psi_n\rangle$, as well as the associated excitation energy $\omega_{n0} \triangleq E_n - E_0$. Moreover, the imaginary part of $\alpha_{zz}(\omega)$ is related with the photoabsorption cross section $\sigma(\omega) \propto \omega \text{Im}\alpha(\omega)$ for visible/ultraviolet/x-ray absorption spectra, which is one of the central quantities considered in designing functional materials.

In the standard FCI-based approach [7,8] for computing $\alpha_{zz}(\omega)$, Eq. (3) is reformulated as

$$\alpha_{zz}(\omega) = \langle \Psi_0 | \hat{z} | \Psi(\omega) \rangle + \langle \Psi_0 | \hat{z} | \Psi(-\omega) \rangle, \quad (4)$$

where the frequency-dependent response wave functions $|\Psi(\pm\omega)\rangle$ are obtained by solving the response equations

$$\hat{Q}[\hat{H}_0 - E_0 \mp (\omega + i\gamma)]\hat{Q}|\Psi(\pm\omega)\rangle = \hat{Q}\hat{z}|\Psi_0\rangle, \quad (5)$$

with the projector $\hat{Q} = 1 - |\Psi_0\rangle\langle\Psi_0|$ in the full N -electron Hilbert space, and hence we avoid the need for determining all excited states in the SOS form (3). The computational complexity of solving Eq. (5) using the best classical iterative algorithm [45] for linear systems of equations scales linearly in the dimension of the N -electron Hilbert space D . For the molecular problem with $\hat{H}_0$ (1), D is exponential in N , e.g., $D = \binom{K}{N}$ with $K = 2N$ for the half-filling case. Therefore, like solving the ground-state eigenvalue problem, viz., $\hat{H}_0|\Psi_0\rangle = E_0|\Psi_0\rangle$, this FCI-based approach scales exponentially in the system size N , and in practice it is limited to very small molecules ($N \lesssim 16$, assuming $K = 2N$) in routine quantum chemistry applications [4,5,8].

Just as QPE and VQE have been applied to the ground-state problem, we attempt to utilize the advantage of quantum algorithms for linear systems of equations [38–44] in computing molecular response properties. However, while QPE can be applied readily to the ground-state problem, both Eqs. (4) and (5) are not in a form that is amenable to computing on

quantum computers directly, due to the asymmetric form of each term in Eq. (4) and the involvement of the projector $\hat{Q}$. To resolve these two problems, we introduce the notation

$$\hat{A}(\pm\omega) \triangleq \hat{H}_0 - E_0 \mp (\omega + i\gamma) \quad (6)$$

for brevity, and we rewrite the first part of $\alpha_{zz}(\omega)$ (4) as

$$\begin{aligned} \langle \Psi_0 | \hat{z} | \Psi(\omega) \rangle &= \langle \Psi_0 | \hat{z} \hat{Q} [\hat{Q} \hat{A}(\omega) \hat{Q}]^{-1} \hat{Q} \hat{z} | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{z} \hat{Q} \hat{A}^{-1}(\omega) \hat{z} | \Psi_0 \rangle \\ &= \langle \Psi_0 | \hat{z} [\hat{A}^\dagger(\omega)]^{-1} \hat{A}^\dagger(\omega) \hat{Q} \hat{A}^{-1}(\omega) \hat{z} | \Psi_0 \rangle, \end{aligned} \quad (7)$$

where the second equality follows from the spectral decompositions $\hat{A}(\omega) = \sum_{n \geq 0} |\Psi_n\rangle [\omega_{n0} - (\omega + i\gamma)] \langle \Psi_n|$ and $\hat{Q} = \sum_{n > 0} |\Psi_n\rangle \langle \Psi_n|$, which immediately imply that $\hat{A}(\omega)$ is invertible for $\gamma > 0$ regardless of ω , and $\hat{Q} [\hat{Q} \hat{A}(\omega) \hat{Q}]^{-1} \hat{Q} = \sum_{n > 0} |\Psi_n\rangle [\omega_{n0} - (\omega + i\gamma)]^{-1} \langle \Psi_n| = \hat{Q} \hat{A}^{-1}(\omega) \hat{Q} = \hat{Q} \hat{A}^{-1}(\omega)$. To reach a symmetric expression, the identity $[\hat{A}^\dagger(\omega)]^{-1} \hat{A}^\dagger(\omega) = 1$ has been inserted in the last line of Eq. (7), which suggests introducing an auxiliary state $|Z(\omega)\rangle$ satisfying an equation similar to Eq. (5) but without the projector $\hat{Q}$,

$$\hat{A}(\omega) |Z(\omega)\rangle = \hat{z} | \Psi_0 \rangle. \quad (8)$$

Consequently, Eq. (7) can be recast into a symmetric form,

$$\langle \Psi_0 | \hat{z} | \Psi(\omega) \rangle = \langle Z(\omega) | \hat{A}^\dagger(\omega) | Z(\omega) \rangle + (\omega - i\gamma) |\langle Z(\omega) | \Psi_0 \rangle|^2. \quad (9)$$

Now the explicit dependence on the projector $\hat{Q}$, which makes the design of a quantum algorithm difficult, has been removed from both the response equation (8) and the expression for the polarizability (9). Its effect is only reflected in the second term of Eq. (9). Likewise, the second part of $\alpha_{zz}(\omega)$ (4) can be expressed in a similar symmetric form,

$$\begin{aligned} \langle \Psi_0 | \hat{z} | \Psi(-\omega) \rangle &= \langle Z(-\omega) | \hat{A}^\dagger(-\omega) | Z(-\omega) \rangle \\ &\quad - (\omega - i\gamma) |\langle Z(-\omega) | \Psi_0 \rangle|^2. \end{aligned} \quad (10)$$

More explicitly, we can separate $\alpha_{zz}(\omega)$ into real and imaginary parts,

$$\begin{aligned} \alpha_{zz}(\omega) &= \text{Re}\alpha_{zz}(\omega) + i \text{Im}\alpha_{zz}(\omega), \\ \text{Re}\alpha_{zz}(\omega) &= \langle Z(\omega) | \hat{H}_0 - E_0 | Z(\omega) \rangle \\ &\quad + \langle Z(-\omega) | \hat{H}_0 - E_0 | Z(-\omega) \rangle - \frac{\omega}{\gamma} \text{Im}\alpha_{zz}(\omega), \\ \text{Im}\alpha_{zz}(\omega) &= \gamma [\langle Z(\omega) | Z(\omega) \rangle - \langle Z(-\omega) | Z(-\omega) \rangle \\ &\quad - |\langle Z(\omega) | \Psi_0 \rangle|^2 + |\langle Z(-\omega) | \Psi_0 \rangle|^2], \end{aligned} \quad (11)$$

where the expected symmetry relations $\text{Re}\alpha_{zz}(-\omega) = \text{Re}\alpha_{zz}(\omega)$ and $\text{Im}\alpha_{zz}(-\omega) = -\text{Im}\alpha_{zz}(\omega)$ are obvious. In fact, from Eq. (8) one can further find $\langle \Psi_0 | \hat{z} | \Psi(\pm\omega) \rangle = \mp \frac{\langle \Psi_0 | \hat{z} | \Psi_0 \rangle}{\omega + i\gamma}$, such that the second terms in Eqs. (9) and (10) will cancel each other in $\alpha_{zz}(\omega)$. Building upon the reformulation of the standard response theory, Eqs. (8)–(11), we are ready to present a quantum algorithm for computing $\alpha_{zz}(\omega)$, using either the quantum linear system algorithms [38–42] or the variational hybrid quantum-classical algorithms [43,44] for solving Eq. (8).

III. QUANTUM ALGORITHM WITH AN EXPONENTIAL SPEEDUP

We assume that the ground-state wave function $|\Psi_0\rangle$ and its associated energy E_0 have been available either by QPE or VQE. The most challenging step for computing $\alpha_{zz}(\omega)$ is to solve the response equation (8), which becomes a linear system of equation with dimension D when expressed in the full many-electron Hilbert space. In this section, we prove that there is a quantum advantage for computing $\alpha_{zz}(\omega)$ on quantum computers over the classical FCI-based approaches [7,8] by using the HHL algorithm as a subroutine [38] to solve Eq. (8).

Since $\hat{A}(\omega)$ (6) in Eq. (8) is non-Hermitian for $\gamma > 0$, $|Z(\omega)\rangle$ can be determined using the HHL algorithm [38] either by

$$\begin{bmatrix} 0 & \hat{A}(\omega) \\ \hat{A}^\dagger(\omega) & 0 \end{bmatrix} \begin{bmatrix} 0 \\ |Z(\omega)\rangle \end{bmatrix} = \begin{bmatrix} \hat{z} | \Psi_0 \rangle \\ 0 \end{bmatrix}, \quad (12)$$

as suggested in the original work [38], or by the following equivalent equation:

$$\hat{A}^\dagger(\omega) \hat{A}(\omega) |Z(\omega)\rangle = \hat{A}^\dagger(\omega) \hat{z} | \Psi_0 \rangle, \quad (13)$$

with a Hermitian matrix on the left-hand side (LHS), which has the same dimension as Eq. (8) at the cost of increasing the condition number. For a linear system of equations $\mathbf{Ax} = \mathbf{b}$, where $\mathbf{A}$ is a Hermitian matrix of dimension D with an eigendecomposition $\mathbf{A} = \mathbf{U}\mathbf{\Lambda}\mathbf{U}^\dagger$, the HHL algorithm [38] essentially prepares a solution following the sequence $\mathbf{x} = \mathbf{U}\mathbf{\Lambda}^{-1}\mathbf{U}^\dagger\mathbf{b}$. The transformation to the eigenbasis of $\mathbf{A}$ and the back-transformation is executed by QPE subroutines [20], which require the implementation of the controlled time evolution $e^{i\mathbf{A}t}$, while the realization of the nonunitary operation $\mathbf{\Lambda}^{-1}$ is through controlled rotations also with the help of ancilla qubits. The runtime complexity of the HHL algorithm is $O(\ln(D)s^2\kappa^2/\epsilon)$ [38], where ϵ is the desired precision, s is the sparsity parameter specifying the maximal number of nonzero entries per row in $\mathbf{A}$, and κ is the condition number of $\mathbf{A}$, i.e., $\kappa = |\lambda_{\max}|/|\lambda_{\min}|$, which is the ratio between the maximal and minimal eigenvalues by moduli of $\mathbf{A}$. The real advantage of the HHL algorithm over classical algorithms depends crucially on the efficiency of four major steps [38,46]: (i) preparation of $\mathbf{b}$ on quantum computers, (ii) Hamiltonian simulation $e^{i\mathbf{A}t}$, (iii) dependence of κ on D , and (iv) readout of the output quantum state $|x\rangle = \mathbf{A}^{-1}|\mathbf{b}\rangle/\|\mathbf{A}^{-1}|\mathbf{b}\rangle\|$ encoding the solution $\mathbf{x}$. Any slowdown in one of the steps could kill the exponential speedup promised by the HHL algorithm. Now we demonstrate how an exponential speedup can be achieved for computing $\alpha_{zz}(\omega)$ on quantum computers by the following algorithm in a step-by-step way:

Step (i): Provided $|\Psi_0\rangle$ is available, the state $\hat{z}|\Psi_0\rangle$ on the right-hand side (RHS) of Eq. (12) or $\hat{A}^\dagger(\omega)\hat{z}|\Psi_0\rangle$ in Eq. (13) can be prepared with a cost of $\text{poly}(N)$ using the linear combination of unitaries (LCU) algorithm [47,48]. This is because both the one-body perturbation $\hat{z}$ (2) and the Hamiltonian $\hat{H}_0$ (1) in $\hat{A}(\omega)$ can be expressed as a sum of $\text{poly}(N)$ Pauli matrices, e.g.,

$$\hat{z} = \sum_{\mu} z_{\mu} P_{\mu}, \quad P_{\mu} = \sigma_{\mu_1} \otimes \sigma_{\mu_2} \otimes \cdots \otimes \sigma_{\mu_K}, \quad (14)$$

where $\sigma_{\mu_k} \in \{I_2, \sigma_x, \sigma_y, \sigma_z\}$ and the number of terms is quadratic in N for $\hat{z}$ (2), through a fermion-to-qubit mapping such as the Jordan-Wigner transformation [49] or the Bravyi-Kitaev transformation [50,51].

Step (ii): Given the RHS of Eq. (12) [or Eq. (13)] prepared on quantum computers, the HHL algorithm is applied to prepare a normalized solution state $|x\rangle = |Z(\omega)\rangle / \sqrt{\langle Z(\omega)|Z(\omega)\rangle}$ for Eq. (8). For molecular systems with $\hat{H}_0$ (1), it is known that the Hamiltonian simulation can be accomplished efficiently in $\text{poly}(N)$, just as in applying QPE to the molecular ground-state problem [13,14,21]. Because $\hat{H}_0$ involves at most two-body Coulomb interactions, the sparsity parameter s is only quartic in N . Thus, the most crucial part for the runtime complexity of the HHL algorithm is the condition number κ . On the one hand, since $\hat{H}_0$ can be written as a sum over $O(N^4)$ Pauli terms $\hat{H}_0 = \sum_{\mu} h_{\mu} P_{\mu}$, as for $\hat{z}$ in Eq. (14), $|\lambda_{\max}|$ of $\hat{H}_0$ [and $\hat{A}(\omega)$] is bounded by a system-dependent constant $\max_{\mu} |h_{\mu}|$ times N^4 . Assuming we consider the scaling with respect to the variation of the system size for systems of the same kind, such as water clusters of different sizes in a given atomic orbital basis set, then $\max_{\mu} |h_{\mu}|$ is independent of N , such that $|\lambda_{\max}|$ is of $\text{poly}(N)$. On the other hand, the operator $\hat{H}_0 - E_0 - \omega$ becomes singular whenever the frequency ω matches the excitation energy ω_{n0} , such that in the worst case $|\lambda_{\min}|$ of $\hat{A}^{\dagger}(\omega)\hat{A}(\omega)$ in Eq. (13) is γ^2 , and likewise for Eq. (12) $|\lambda_{\min}|$ equals γ . In practice, the parameter γ is a fixed input parameter for spectral resolution, which determines the half-width at half-maximum (HWHM) of peaks in $\text{Im}\alpha(\omega)$ (11). Thus, the condition numbers κ for the coefficient matrices in Eqs. (12) and (13) are polynomial in the system size N instead of the dimension of the Hilbert space D , which is exponential in N . This leads to the conclusion that the runtime complexity of the HHL algorithm for preparing the normalized solution state $|x\rangle$ from either Eq. (12) or (13) is $\text{poly}(N)$.

Step (iii): After applying the HHL algorithm to Eq. (12) or (13), the first part of $\alpha_{zz}(\omega)$ (4) can be computed from $|x\rangle$ using Eq. (9) in $\text{poly}(N)$, without accessing its individual entry. This is achieved by first noting that the norm of $|Z(\omega)\rangle$ required in Eq. (9) can be computed using Eq. (8) as

$$\langle Z(\omega)|Z(\omega)\rangle = \langle \Psi_0|\hat{z}\hat{z}|\Psi_0\rangle / \langle x|\hat{A}^{\dagger}(\omega)\hat{A}(\omega)|x\rangle, \quad (15)$$

which only requires the measurements of $\langle \Psi_0|\hat{z}\hat{z}|\Psi_0\rangle$ and $\langle x|\hat{A}^{\dagger}(\omega)\hat{A}(\omega)|x\rangle$. Since the number of measurements is proportional to the number of terms [29,52] in $\hat{z}$ and $\hat{A}^{\dagger}(\omega)\hat{A}(\omega)$, the cost scales polynomially in N . Then, the first term in Eq. (9) involving $\langle Z(\omega)|\hat{H}_0|Z(\omega)\rangle$ can be obtained from the measurement of $\langle x|\hat{H}_0|x\rangle = \sum_{\mu} h_{\mu} \langle x|P_{\mu}|x\rangle$ in the same way as obtaining the energy in VQE [28,29], while the second term $|\langle Z(\omega)|\Psi_0\rangle|^2$ can be computed from $|\langle x|\Psi_0\rangle|^2$ by the SWAP test [53,54] or simply from $\frac{|\langle \Psi_0|\hat{z}|\Psi_0\rangle|^2}{\omega^2 + \gamma^2}$ following Eq. (8). Therefore, the necessary information for computing $\alpha_{zz}(\omega)$ from the output state $|x\rangle$ of the HHL algorithm [and its counterpart for $|Z(-\omega)\rangle$] can be accessed through $\langle x|\hat{H}_0^2|x\rangle$, $\langle x|\hat{H}_0|x\rangle$, and $|\langle x|\Psi_0\rangle|^2$ with a cost of $\text{poly}(N)$.

Using the above procedure, we show that the dynamic polarizability tensor $\alpha_{zz}(\omega)$ of molecules can be computed on quantum computers with $\text{poly}(N)$ runtime complexity, achieving an exponential speedup compared with the classical FCI-based approach [7,8]. This becomes possible due to the

specialities of the molecular response problem, such that all the limitations of the HHL algorithm can be overcome in this application: the RHS of Eq. (8) can always be efficiently prepared given $|\Psi_0\rangle$, $e^{i\hat{H}_0 t}$ can be efficiently simulated due to the sparse structure of $\hat{H}_0$ (1), the condition numbers κ for matrices in Eqs. (12) and (13) are polynomial in N , and finally only partial information of the solution is required for computing $\alpha_{zz}(\omega)$. Therefore, the molecular response problem is an ideal application of the HHL algorithm [38], and the same conclusion is also generalizable to its improved variants [39–41].

IV. VARIATIONAL HYBRID QUANTUM-CLASSICAL ALGORITHM

While the above HHL-based quantum variant of our algorithm has a theoretically provable quantum advantage, it is considered to be a long-term algorithm in the sense that in general it requires a long circuit depth and is less suitable for NISQ devices, even though there has been recent experimental progress on realizing the HHL algorithm itself on small-scale problems [55–58]. To enable the computation of molecular response properties for potentially interesting larger molecules on near-term devices, here we introduce a variational hybrid quantum-classical variant by combining the same theoretical framework with the variational hybrid quantum-classical algorithms for linear systems of equations [43,44], which, like the VQE algorithm [28,29], have much less of a requirement for circuit depth and are more robust against noises due to the variational nature.

Specifically, suppose the ground state has been obtained by VQE through a variational parametrization $|\Psi_0\rangle = U(\theta_0)|0\rangle$, where $U(\theta_0)$ represents a parametrized unitary circuit with parameters θ_0 , such as the unitary coupled cluster (UCC) ansatz [28] or the hardware efficient ansatz [32]. Instead of solving Eq. (8) for $|Z(\omega)\rangle$ using the HHL algorithm, we can design a parametrized ansatz for the normalized state $|\theta\rangle = |Z(\omega)\rangle / \sqrt{\langle Z(\omega)|Z(\omega)\rangle} = U_Z(\theta)|0\rangle$. Then, the solution of Eq. (8) can be found by minimizing the following cost function:

$$\mathcal{C}(\theta) = \langle \Psi_0|\hat{z}\hat{z}|\Psi_0\rangle \langle \theta|\hat{A}^{\dagger}(\omega)\hat{A}(\omega)|\theta\rangle - |\langle \Psi_0|\hat{z}\hat{A}(\omega)|\theta\rangle|^2, \quad (16)$$

with $\mathcal{C}(\theta) \geq 0$ due to the Cauchy-Schwarz inequality. Since $\hat{A}(\omega)$ is always nonsingular for $\gamma > 0$ regardless of ω , the solution of Eq. (8) is uniquely determined by the condition $\mathcal{C}_{\min}(\theta) = 0$. The two symmetric terms $\langle \Psi_0|\hat{z}\hat{z}|\Psi_0\rangle$ and $\langle \theta|\hat{A}^{\dagger}(\omega)\hat{A}(\omega)|\theta\rangle$ in Eq. (16) are exactly those appearing in Eq. (15), and hence they can be evaluated in the same way through measurements after preparing $|\Psi_0\rangle$ and $|\theta\rangle$, respectively. The overlap term can be rewritten as $\langle \Psi_0|\hat{z}\hat{A}(\omega)|\theta\rangle = \langle 0|U^{\dagger}(\theta_0)\hat{z}\hat{A}(\omega)U_Z(\theta)|0\rangle = \sum_{\mu} \zeta_{\mu} \langle 0|U^{\dagger}(\theta_0)P_{\mu}U_Z(\theta)|0\rangle$, where the expansions of $\hat{z}$ (14) and $\hat{A}(\omega)$ were used to obtain an expansion $\hat{z}\hat{A}(\omega) = \sum_{\mu} \zeta_{\mu} P_{\mu}$. Terms like $\langle 0|U^{\dagger}(\theta_0)P_{\mu}U_Z(\theta)|0\rangle$ can be computed in multiple ways, with the simplest choice being the standard Hadamard test. It should be pointed out that improved techniques [43,44] have been proposed for defining better cost functions and evaluating the overlap term with reduced requirements on the number of controlled operations. Finally, once $|\theta\rangle$ has been determined variationally, $\alpha_{zz}(\omega)$ (11) can

be computed in exactly the same way following step (iii) in the previous section. In practice, errors in computing $\mathcal{C}(\theta)$ and $\alpha_{zz}(\omega)$ due to noises can be mitigated using the available techniques [59–63] developed for VQE to achieve better accuracy. Thus, together with the VQE algorithm [28,29] for the ground state $|\Psi_0\rangle$, this variational hybrid quantum-classical variant provides a more practical way of computing molecular response properties on near-term devices.

V. EXTENSIONS TO GENERAL RESPONSE PROPERTIES

Both variants of the proposed algorithm can be generalized to compute general linear and nonlinear response properties using the same idea of first deriving a symmetric expression for the target property by introducing appropriate auxiliary states, and then determining these states by solving response equations with appropriate quantum or hybrid algorithms. For off-diagonal components of $\alpha_{ij}(\omega)$, e.g., $\alpha_{xz}(\omega)$ containing a form of $\langle\Psi_0|\hat{x}\hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}\hat{z}|\Psi_0\rangle$, a symmetric expression can be derived by applying the polarization identity, which involves a linear combination of four symmetric terms $\langle\Psi_0|[\hat{x} \pm (i)\hat{z}]^\dagger \hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}[\hat{x} \pm (i)\hat{z}]|\Psi_0\rangle$, viz.,

$$\begin{aligned} & \text{Re}\langle\Psi_0|\hat{x}\hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}\hat{z}|\Psi_0\rangle \\ &= \frac{1}{4}\{\langle\Psi_0|(\hat{x} + \hat{z})^\dagger \hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}(\hat{x} + \hat{z})|\Psi_0\rangle \\ & \quad - \langle\Psi_0|(\hat{x} - \hat{z})^\dagger \hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}(\hat{x} - \hat{z})|\Psi_0\rangle\} \quad (17) \end{aligned}$$

and

$$\begin{aligned} & \text{Im}\langle\Psi_0|\hat{x}\hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}\hat{z}|\Psi_0\rangle \\ &= -\frac{1}{4}\{\langle\Psi_0|(\hat{x} + i\hat{z})^\dagger \hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}(\hat{x} + i\hat{z})|\Psi_0\rangle \\ & \quad - \langle\Psi_0|(\hat{x} - i\hat{z})^\dagger \hat{Q}[\hat{Q}\hat{A}(\omega)\hat{Q}]^{-1}\hat{Q}(\hat{x} - i\hat{z})|\Psi_0\rangle\}. \quad (18) \end{aligned}$$

Each of them can be computed using the same algorithm for $\alpha_{zz}(\omega)$. As an important example for nonlinear response functions, we consider the resonant inelastic x-ray scattering (RIXS) amplitudes [5,64] for probing elementary excitations in complex correlated electron systems. It is given by the Kramers-Heisenberg formula [65]

$$\begin{aligned} \mathcal{F}_{zz}^{f0}(\omega) &= \sum_n \left[\frac{\langle\Psi_f|\hat{z}|\Psi_n\rangle\langle\Psi_n|\hat{z}|\Psi_0\rangle}{\omega_{n0} - (\omega + i\gamma)} \right. \\ & \quad \left. + \frac{\langle\Psi_f|\hat{z}|\Psi_n\rangle\langle\Psi_n|\hat{z}|\Psi_0\rangle}{\omega_{n0} + (\omega' + i\gamma)} \right], \quad (19) \end{aligned}$$

where $\omega' \triangleq \omega - \omega_{f0}$, and $|\Psi_f\rangle$ represents the final state of interest involved in the inelastic scattering process. Since Eq. (19) takes a similar form to Eq. (3) for $\alpha_{zz}(\omega)$, a similar strategy can be designed to compute the scattering cross section $|\mathcal{F}_{zz}^{f0}(\omega)|^2$ [64]. In particular, within the rotating wave approximation, where the second term of Eq. (19) is neglected, the scattering cross section is simply given by $|\mathcal{F}_{zz}^{f0}(\omega)|^2 = |\langle\Psi_f|\hat{z}|Z(\omega)\rangle|^2$ with the same $|Z(\omega)\rangle$ in Eq. (8), which can be computed by modifications of the SWAP test [53].

In summary, we presented a general algorithm for computing the molecular response properties on quantum computers. The most demanding step involves a set of linear systems of equations for auxiliary quantum states, which can be solved either by quantum algorithms [38–42] or variational hybrid quantum-classical algorithms [43,44]. The resulting two variants enable the computation of molecular response properties for frequencies of interest directly. While the latter variational hybrid variant is more suitable for near-term applications, we showed that the former with the HHL algorithm [38] as a subroutine has a provable quantum speedup over the existing classical FCI-based approach [7,8]. Our work provides theoretical evidence that quantum chemistry is a promising area that will benefit from quantum computation. Enabling accurate and efficient predictions of molecular response properties on quantum computers will potentially open up a broad range of new applications of quantum computation in material science and drug discovery in the near future.

Note added. During the review process of this work, we became aware of a related work [66] in which a different algorithm was proposed for constructing the linear-response functions of molecules via quantum phase estimation and statistical sampling.

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