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A posteriori corrections to the iterative qubit coupled cluster method to minimize the use of quantum resources in large-scale calculations

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Abstract
The iterative qubit coupled cluster (iQCC) method is a systematic variational approach to solve the electronic structure problem on universal quantum computers. It is able to use arbitrarily shallow quantum circuits at expense of iterative canonical transformation of the Hamiltonian and rebuilding a circuit. Here we present a variety of a posteriori corrections to the iQCC energies to reduce the number of iterations to achieve the desired accuracy. Our energy corrections are based on a low-order perturbation theory series that can be efficiently evaluated on a classical computer. Moreover, capturing a part of the total energy perturbatively, allows us to formulate the qubit active-space concept, in which only a subset of all qubits is treated variationally. As a result, further reduction of quantum resource requirements is achieved. We demonstrate the utility and efficiency of our approach numerically on the examples of 10-qubit N2 molecule dissociation, the 24-qubit H2O symmetric stretch, and 56-qubit singlet-triplet gap calculations for the technologically important complex, tris-(2-phenylpyridine)iridium(III) Ir(ppy)3.

1. Introduction

Electronic structure calculations [1] on universal-gate noisy intermediate-scale quantum (NISQ) [2] devices are challenging because of the limited number of qubits, limited connectivity, short coherence times, and noisy measurements. In view of these limitations, algorithms based on the variational quantum eigensolver (VQE) framework [3, 4], a hybrid quantum–classical variational scheme, show the most promise. Central to VQE is a unitary $\hat{U}(\tau)$, where $\tau$ is a vector of numerical parameters, acting on an initial state of a quantum register (an initial wavefunction) $|0\rangle$. Once $\hat{U}(\tau)$ is fixed, the variational energy estimate

$$E(\tau) = \langle 0 | \hat{U}^\dagger(\tau) \hat{H} \hat{U}(\tau) | 0 \rangle,$$  

is evaluated on a quantum computer by measuring terms (or groups of terms) [5–12] of the qubit Hamiltonian

$$\hat{H} = \sum_k C_k \hat{P}_k,$$  

where $C_k$ are numerical coefficients determined by the electronic Hamiltonian of a problem, and

$$\hat{P}_k = \prod_i \hat{\sigma}^{(k)}_i$$  

are strings of Pauli elementary operators $\hat{\sigma}_i \in \{\hat{x}_i, \hat{y}_i, \hat{z}_i\}$ acting on the $i$th, $i = 1, \ldots, n$, qubit [13]. We call these strings ‘Pauli words’ for brevity. The values of $E(\tau)$ are used by a classical computer to update
amplitudes $\tau$ in the direction that lowers the energy. This processes is repeated until the variational minimum of energy is obtained.

The ansatz for $\hat{U}(\tau)$ must satisfy certain requirements. First, it must be either directly represented as a sequence of quantum gates or readily converted to it. Secondly, it has to be accurate already for the small number of variational parameters and demonstrate rapid convergence with increasing the number of them. Finally, it must be systematically improvable. Several forms of $\hat{U}(\tau)$ were explored in literature. The ‘hardware-efficient’ form [14, 15] encodes $\hat{U}(\tau)$ directly as a set of gates available on a particular hardware platform, but by far the most popular approach is based on the unitary coupled cluster (UCC) ansatz and its generalizations [3, 16–21],

$$\hat{U}(\tau) = e^{\hat{T}(\tau) - \hat{T}(\tau)^\dagger},$$  \hspace{1cm} (4)

where $\hat{T}(\tau)$ is a parametrized cluster operator, and $\hat{T}(\tau)^\dagger$ is its Hermitian conjugate. To be used in VQE, the UCC ansatz must be first converted to a product form,

$$\hat{U}(\tau) = \prod_j \exp(-ir_j\hat{P}_j/2)$$ \hspace{1cm} (5)

in which the generators, Pauli words $P_j$, are inferred from $\hat{T}_K$ and $\hat{T}_K^\dagger$. The difficulty is that $\hat{T}_K$ and $\hat{T}_K^\dagger$ are non-commuting so that after transformation to the qubit space, the ansatz (5) is order-dependent [22, 23].

Recently, the VQE-based methods that started with the form (5) directly were proposed [24–26]. For such direct methods the main challenge is finding generators that provide fast and systematic convergence. A simple random sampling of generators (among $4^n - 1$ possible) is highly inefficient due to the so-called barren plateaus [27]. Additionally, as was shown for the polynomially-large fixed-rank fermionic excitation spaces, systematic convergence is warranted only if operators are allowed to be sampled more than once [22]. The repeated sampling is a strategy adopted by the ADAPT-VQE method [25]. It uses the set of unitary coupled cluster singles and doubles (UCCSD) fermionic excitation operators converted to the qubit representation as a set of generators, which are included into the unitary (5) after ranking them by a gradient-based procedure carried out on a quantum device. ADAPT-VQE requires the full re-optimization of the entire unitary each time new operators are appended, which quickly becomes cumbersome. The iterative qubit coupled cluster (iQCC) method [26] completely abandons the fermionic excitation picture and works in the qubit operator space. It introduces the concept of the direct interaction set (DIS)—a collection of all possible operators that guarantees the first-order energy lowering being included in the ansatz (5). The DIS can be efficiently constructed on a classical computer. The iQCC method also uses the iterative approach, but instead of (re)-optimization of a lengthy and potentially intractable unitary, a shorter $\hat{U}^{(0)}$ is constructed based on the current DIS, its parameters are optimized, and both $\hat{U}^{(0)}$ and optimal $\tau^0$ are used to transform (dress) the current Hamiltonian $\hat{H}^{(0)}$ to define a new one,

$$\hat{H}^{(0+1)} = (\hat{U}^{(0)}(\tau^0))^\dagger \hat{H}^{(0)} \hat{U}^{(0)}(\tau^0),$$  \hspace{1cm} (6)

for which the procedure of finding the DIS is repeated. It was numerically demonstrated that such a procedure eventually converged to the exact ground-state energy even if a single top-ranked generator from the DIS was used to build $\hat{U}^{(0)}$. Thus, it is possible to use arbitrarily shallow quantum circuits at expense of additional dressing steps carried out on a classical computer and additional quantum measurements of intermediate $\hat{H}^{(0)}$.

The iQCC method implemented without a quantum computer (e.g. on a classical simulator) can be seen as a variant of iterative and selected-configuration interaction (CI) techniques that have recently received a great deal of attention in the traditional quantum chemistry [28–32]. Indeed, iQCC approaches the full configurational interaction (FCI) [or the complete active space configurational interaction (CASI)] limit iteratively by repeating selecting/optimization/dressing cycles. Contrary to the matrix diagonalization approaches, iQCC provides both variational and size-consistent estimate to the FCI energy at every iteration (see section 4.1). The canonical transformation step [‘iQCC dressing’, equation (6)] mostly resembles the ‘numerical canonical transformation approach’ by White [33], but is performed in a qubit, rather than fermionic, operator space. Using Pauli words as generators of unitary transformations allows for the exact truncation of the Baker–Campbell–Hausdorff expansion at the second order for each generator. Provided that the generators are selected according to their projected importance for the energy lowering, iQCC systematically approaches the exact energy. This conceptually distiguishes it from other methods exploiting canonical transformations, which eventually enforce some sort of closure approximations to avoid dealing with high-rank (higher than doubles) fermionic operators [34], although in some special cases canonical (similarity) transformations can be evaluated without truncation [35].
emphasized that high-rank operators (in terms of coupled qubits, or, equivalently, the length of Pauli words) are ubiquitous in the qubit representation due to the non-linear nature of fermion-to-qubit transformations, which makes the length (number of terms), not the rank, a primary measure of operator’s complexity.

The major obstacle for the original iQCC method is the exponential growth of intermediate Hamiltonians with the number of generators included into the qubit coupled cluster (QCC) form (5) and the number of steps. While operator compression and energy extrapolation was suggested in reference [26] as mitigation techniques, both of them were only moderately efficient. The recent proposal [36] addresses the problem of exponential growth of the QCC form by exploiting freedom in definition of the DIS: it introduces involutary combinations of anti-commuting Pauli generators to turn an exponential growth into merely linear. While this approach potentially allows for classical optimization of much lengthier QCC unitaries, it is still limited by $O(n^3)$ terms in involutary combinations, so that several iterations may still be necessary to achieve the desired accuracy. In this work we seek for reducing the number of iQCC iterations by devising a posteriori completeness corrections to the iQCC energies, which can be efficiently evaluated on a classical computer. Obviously, this saves quantum resources. Moreover, capturing a bulk of contributions to the exact energy classically allows us to consider the QCC form (5), in which only a subset of all qubits is considered explicitly, thus enabling the active-space treatment.

Classical post-processing has already been explored in the context of the electronic structure problem on quantum computers. Takeshita et al [37] suggested to measure matrix elements of the Hamiltonian in the basis of expansion operators which provide additional flexibility to a wave function encoded by a quantum circuit. Operationally, this amounts to measuring selected elements of high-order density matrices followed by diagonalization on a classical computer. In our approach we compute additional matrix elements of the Hamiltonian with operators from the DIS classically. Likewise, it is possible to formulate a linear variational problem and solve it via diagonalization on a classical computer. However, a computationally more efficient solution is to use a perturbation theory. We exploit the fact that the iQCC method systematically reduces the discrepancy between the expectation value of the QCC energy, equation (1), evaluated with the dressed Hamiltonian $H^{(0)}$ and the exact energy. This process may be interpreted as iterative construction of the operator $H^{(\infty)}$, for which the reference state $|0\rangle$ is an eigenvector with the exact energy as an eigenvalue. After the finite number of iQCC iterations, $|0\rangle$ becomes sufficiently close to the exact eigenvector, and the idea to apply a perturbation theory emerges naturally. Moreover, if the perturbative treatment fails, additional iQCC cycles can be completed to make a perturbation smaller.

The perturbation theory is widely used to improve efficiency of CI techniques [29–31, 38–41]. In many cases it serves a dual purpose: first, to select basis vectors (e.g. Slater determinants) that are important for energy lowering and second, to extrapolate CI energies to the full-CI limit [42, 43]. In what follows we derive a perturbation theory and the related linear variational problem for qubit Hamiltonians, which can also be used to rank generators, as well as to extrapolate QCC energies to the full-CI limit. First, we introduce a new normal form for qubit Hamiltonians, which bears some similarity with the normal-ordered fermion operators. Then, we give an algebraic definition of the DIS, and finally, discuss various variational and perturbative completeness corrections to the QCC energies. The theoretical section ends with the description of the active-space modification of iQCC. Subsequently, we numerically assess the utility and performance of the proposed modifications on three model problems: 10-qubit N2 molecule dissociation, the 24-qubit H2O symmetric stretch, and 56-qubit singlet-triplet gap calculations for the tris-(2-phenylpyridine)iridium(III), Ir(ppy)₃ molecule.

2. Theory

2.1. Normal-ordered qubit Hamiltonians

The qubit Hamiltonian, equation (2), is a simple linear combination of Pauli words. Although this form is very general, it does not offer any advantage for evaluation of the quantum–mechanical expectation values, like those appearing in VQE, equation (1). Here we derive a special form which, on the one hand, leads to simple rules for evaluating expectation values, and, on the other, provides an algebraic view on the DIS. The new normal form resembles the fermionic normal order, while the rules are reminiscent the Slater–Condon rules [1].

Any qubit Hamiltonian (2) can always be written as

$$\hat{H} = \sum_k C_k \hat{Z}_k \hat{X}_k,$$

(7)

where $Z_k = z_{k1} \cdots z_{kn}$ and $X_k = x_{k1} \cdots x_{kn}$ are Pauli words containing $\hat{z}$ or $\hat{x}$ operators only. The representation (7) follows from the fact that $\hat{z}$ and $\hat{x}$ operators together with the imaginary unit $i$ are the
generators of the Pauli group, since \( \hat{y} = -i\hat{z}\hat{x} \) and \( \hat{x}^2 = \hat{y}^2 = 1 \), where \( \hat{e} \) is the identity operator. To obtain equation (7) from equation (2) one must replace all occurrences of \( \hat{y}_j \) with \( -i\hat{z}_i\hat{x}_j \) in every \( \hat{P}_k \) and collect \( \hat{z}_i' \) and \( \hat{x}_j' \) in factors \( \hat{Z}_i' \) and \( \hat{X}_j' \) respectively. The multi-indices \([k'_1, \ldots, k'_m]\) and \([k_1, \ldots, k_n]\) may overlap; the common indices correspond to the \( \hat{y} \) operators in these positions. The coefficients \( \bar{C}_k \) in equation (8) may differ from \( C_k \) in an additional phase factor \((\pm 1, \pm i)\), depending on the number of \( \hat{y} \) factors in the corresponding \( \hat{P}_k \).

Together with the ZX ('right') expansion one may define an alternative XZ ('left') expansion as

\[
\hat{H} = \sum_k \bar{C}_k \hat{X}_k \hat{Z}_k. 
\]  

(8)

The operator factors \( \hat{X}_k' \) and \( \hat{Z}_k \) are identical between the 'right' and the 'left' variants, but the corresponding coefficients may have different signs \( \bar{C}_k = \pm C_k \). However, as long as all \( \hat{P}_k \)-s contain the even number of \( \hat{y} \) factors, the coefficients are identical. Such hermitian Hamiltonians with the even number of \( \hat{y} \) have real matrix elements in a real basis set. In fact, all electronic Hamiltonians in the absence of magnetic fields and spin-orbital interaction are of this kind.

Expansion (7) can be regrouped as

\[
\hat{H} = \hat{I}_k(\hat{x}) + \sum_k \hat{I}_k(\hat{z})\hat{X}_k, 
\]  

(9)

where \( \hat{I}_k(\hat{x}) = \hat{I}_k(\hat{z}_1, \hat{z}_2, \ldots) \) are generalized Ising Hamiltonians containing only the products of \( \hat{z}_j \) operators. We assume that \( k \) is an integer whose binary representation matches the string of Pauli elementary \( \hat{x} \) operators such that 1 in the \( i \)th position indicates the presence of \( \hat{x}_i \).

Imagine now that \( \hat{H} \) acts on a direct-product \( n \)-qubit wavefunction,

\[
|\Phi\rangle = |\pm 1\rangle_1 \cdots |\pm 1\rangle_n, 
\]  

(10)

where \( |\pm 1\rangle \) is the eigenstate of \( \hat{z}_j \) operator with eigenvalues \(+1\) or \(-1\). There are \( 2^n \) of such states which correspond to distinct strings of \(+1\) and \(-1\). These linearly-independent states were called the perfect mean-filed states in reference \([26]\). Every product state is an eigenstate of an arbitrary Ising Hamiltonian, whereas Pauli strings \( \hat{X}_k \) map one mean-field state into another. That is, the expectation value of an Ising Hamiltonian \( \hat{I}_k(\hat{x}) \) on an arbitrary mean-field state \( |0\rangle \) is, in general, non-zero,

\[
\omega_k = |\langle 0|\hat{I}_k(\hat{x})|0\rangle| \neq 0, 
\]  

(11)

whereas

\[
\langle 0|\hat{X}_k|0\rangle = 0, \quad k > 0. 
\]  

(12)

Equations (11) and (12) are the analogs of the Slater–Condon rules.

### 2.2. Algebraic definition of the direct interaction set

The DIS was defined in reference \([26]\) as a set of operators satisfying \( \frac{dE}{d\tau} \neq 0 \), where

\[
E(\tau) = \langle 0|e^{i\tau\hat{P}/2} \hat{H} e^{-i\tau\hat{P}/2} |0\rangle, 
\]  

(13)

\[
\frac{dE}{d\tau} \bigg|_{\tau=0} = -\frac{i}{2} \langle 0| \{\hat{H}, \hat{P}\} |0\rangle. 
\]  

(14)

The reference state \( |0\rangle \) is assumed to be a perfect mean-field state, equation (10). Using the normal-ordered form (9) we can write for the energy derivative:

\[
\frac{|dE|}{d\tau} \leq \sum_{k>0} \omega_k \left| \frac{1}{2i} \langle 0| [\hat{X}_k, \hat{P}] |0\rangle \right| = \sum_{k>0} \omega_k |\text{Im}\langle 0|\hat{X}_k\hat{P}|0\rangle| 
\]  

(15)
Terms in equation (15) are algebraically independent; hence, at least one of them must be non-zero, which in view of equations (11) and (12) implies that

\[ \hat{X}_i \hat{P} = \hat{Z}_{k'}, \]  

(16)

where \( k' \) runs from 1 to \( 2^n \). To guarantee that the imaginary part of the lhs of equation (16) is non-zero, \( k' \) is additionally subjected to a constraint that \( k' \) and \( k \) must intersect in an odd number of bits, which leaves \( 2^{n-1} \) variants for \( k' \). Equation (16) can be easily solved by multiplying both sides by \( \hat{X}_k \):

\[ \hat{P}_{kk'} = \hat{X}_k \hat{Z}_{k'}. \]  

(17)

Such defined \( \hat{P}_{kk'} \) will contain the odd number of \( \hat{y} \) and satisfy

\[ \frac{dE[\hat{P}_{kk'}]}{d\tau} = \omega_k |\langle 0|\hat{Z}_{k'}|0\rangle| = \omega_k. \]  

(18)

Thus, the DIS is a set of solutions of equation (16) with indices \( k \) coming from the expansion (9) and \( k' \) subjected the condition above. Different \( k \) characterize different groups of operators in the DIS with different values of gradients \( \omega_k \), whereas different \( k' \) label operators with the identical gradients; in other words, the DIS can be described as a union of groups of operators. In reference [26] the binary representation of each \( k \) was called the flip set with respect to a mean-field reference \( |0\rangle \). In what follows we drop the primed indices on the generators from the DIS, assuming that we always deal with some fixed representative of the corresponding group. Taking a different representative introduces an extra phase factor to matrix elements, namely, \( \langle 0|\hat{A}\hat{P}_k|0\rangle = (\pm 1, \pm i)|\langle 0|\hat{A}\hat{X}_k|0\rangle| \), for an arbitrary \( \hat{A} \) and a selected representative \( \hat{P}_k \) from the \( k \)th DIS group.

We note that for a general non-mean-field state \( |0\rangle \), the condition (12) no longer holds, and operators outside the DIS acquire non-zero gradients as well. This forced authors of reference [26] to search for a ‘nearest’ mean-field solution with an unclear impact on the ranking. Defining the DIS through the expansion (9) as a set of operators satisfying equation (16) provides a reference-independent, algebraic view on it.

2.3. Linear variational ansatz for a qubit wavefunction

\( 2^n \) distinct Pauli generators \( \hat{X}_k \) map a fixed mean-field state \( |0\rangle \) into different \( n \)-qubit mean-field states, \( |k\rangle = \hat{X}_k|0\rangle \) for \( k = 1, \ldots, 2^n \), which constitute a basis in the Hilbert space of \( n \)-qubit wave functions. Thus, for an arbitrary state \( |\Psi\rangle \) one can write:

\[ |\Psi\rangle = \left( 1 + \sum_{k>0} d_k \hat{X}_k \right) |0\rangle \]  

(19)

(the intermediate normalization \( \langle 0|\Psi\rangle = 1 \) is assumed), where \( d_k \) are expansion coefficients.

The linear variational ansatz (19) is naturally associated with the matrix eigenvalue problem

\[ \hat{H}d = Ed, \]  

(20)

with the matrix \( \hat{H} = \{ \langle 0|\hat{X}_k\hat{H}\hat{X}_j|0\rangle \}_{k,j=0}^M \) where \( M \leq 2^n \), \( d = \{ d_k \}_{k=0}^M \) is an eigenvector.

Equation (20) can be solved on a classical computer to get corrected ground-state energy. If all \( 2^n \) operators are used, this results in the exact ground-state energy and wave function. The procedure, however, is equivalent to FCI and, hence, intractable. A more convenient way is to include all mean-field states that are directly coupled to \( |0\rangle \). Consider the 0th row of the Hamiltonian matrix \( \hat{H} \):

\[ H_{0j} = \langle 0|\hat{H}\hat{X}_j|0\rangle. \]  

(21)

If these matrix elements are required to be non-zero, then the set of the corresponding \( \hat{X}_j \) matches the group structure of the DIS. If any representative \( \hat{P}_k \) (see equation (17)) is used in place of \( \hat{X}_k \), an additional phase factor appears in front of \( d_k \), but the solution of the matrix eigenvalue problem (20) remains the same, which explains the operator redundancy of the DIS.

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4 Strictly speaking, the condition must be written as

\[ \hat{X}_i \hat{P} = \hat{I}_k(z) \]

where \( \hat{I}_k(z) \) is a new generalized Ising Hamiltonian. It can be chosen arbitrarily, for example, to make the resulting generator commuting with global symmetry operators, such as the electron number \( \hat{N} \) or the total spin-squared \( \hat{S}^2 \) ones. Additionally, this operator can be made unimodular, i.e. \( \langle 0|\hat{I}_k|0\rangle = 1 \).
The row \( H_{0j}, j > 0 \) is evaluated as a part of the iQCC ranking procedure \([26]\). To complete the
collection of whole Hamiltonian matrix \( H \), one needs to compute remaining matrix elements
\( \langle 0|X_j \hat{H} X_j|0 \rangle \) for \( i,j > 0 \) and \( i,j \in \text{DIS} \). This procedure is quadratic in the number of groups in the DIS.

The eigenproblem \((20)\) with the qubit Hamiltonian derived from the second-quantized counterpart
using the Jordan–Wigner (JW) mapping and operators sampled from the DIS is equivalent to the
configuration-interaction with singles and doubles (CISD). There is one-to-one correspondence between
Slater determinants and qubit mean-field states, so all the states that have non-zero matrix elements with
the ground state, on the one hand, are singly- and doubly-excited Slater determinants (according to
Slater–Condon rules), on the other, are the qubit mean-field states \( |k \rangle = \hat{X}_k|0 \rangle \) with \( \hat{X}_k \) sampled from the
DIS. If, however, \( \hat{H} \) is a dressed operator at the \( i \)th iQCC step, its DIS contains selected high-rank coupling
operators, whose interpretation in terms of fermion excitations is unclear.

2.4. Perturbation theory

Variational improvement of iQCC energies by equation \((20)\) may still be too computationally demanding as
the full diagonalization of \( H \) scales cubically with the size of the DIS. Moreover, when iQCC energies
approach the exact, corrections become smaller, which naturally calls for perturbation-theory
consideration. The simplest solution is based on the Epstein–Nesbet perturbation theory (ENPT), in which
energy denominators. Energy derivatives \( \omega_j \) are readily available at the end of each iQCC iterations,
while \( D_j \) can be computed with an overhead which is strictly linear in the size of the DIS.

The second-order ENPT correction equation \((23)\) diverges when \( D_j \to 0 \). In this case an analog of the
degeneracy-corrected perturbation theory \([46]\) can be derived (see appendix A), giving rise to the formula

\[
\Delta E_{\text{DUC}} = \sum_j \left( \frac{D_j}{2} - \sqrt{\left( \frac{D_j}{2} \right)^2 + \omega_j^2} \right),
\]

where DUC stands for the ‘diagonal unitary correction’. For small couplings \( \omega_j \), \( E_{\text{DUC}} \) approaches the
ENPT2 correction \((23)\) but remains finite as \( D_j \to 0 \).

2.5. Combined variational-perturbative correction

Being computational efficient, the perturbation theory may still fail in the case of a small ground-excited
energy gap; the variational correction is more robust but computationally demanding. To combine virtues
of both we merge them into a single computational framework. We rewrite the full matrix problem \((20)\) as
two smaller sub-problems in a spirit of the Löwding partitioning \([47]\):

\[
\begin{align*}
\mathbf{h} p + \mathbf{b}^\dagger \mathbf{q} &= E p \\
\mathbf{b} p + C \mathbf{q} &= E \mathbf{q},
\end{align*}
\]

where \( \mathbf{h} \) is a \( m \times m \) submatrix of \( H \), \( \mathbf{b}^\dagger \) is the remaining upper right part, and \( C \) is a matrix with the
mean-field energies \((22)\) on diagonals. \( 1 \leq m \leq N + 1 \), where \( N \) is the number of groups in the DIS, and
the first state is the ground-state reference \( |0 \rangle \), \( p \) and \( q \) are first \( m \) and remaining \( N + 1 - m \) components of the
full eigenvector \( \mathbf{d} \) (see equation \((20)\)), respectively. If \( E \) is an eigenstate, we can solve equation \((27)\) for \( q \)
and plug it into equation \((26)\) to obtain

\[
\mathbf{h}_{\text{eff}}(E) p = E p,
\]

where

\[
\mathbf{h}_{\text{eff}}(E) = \mathbf{h} + \Sigma(E).
\]

is the matrix of the effective energy-dependent Hamiltonian, and

\[
\Sigma(E) = -\mathbf{b}^\dagger (C - E)^{-1} \mathbf{b}
\]
is the self-energy. If \( m = N + 1 \), the self-energy vanishes and the problem (28) reduces to the original matrix formulation (20). In the opposite limit, \( m = 1 \), equation (28) is a non-linear equation, which, nevertheless, can be solved for the exact ground-state energy provided that the self-energy is exact. However, as follows from equation (30), this amounts to full inversion of the \((C - E)\) matrix, which costs similarly to diagonalization. The inversion is trivial though, if only the diagonal matrix elements of \( C \) are retained; the self-energy can be computed in this case via simple multiplication of \( b^\dagger \) and \((C - E)^{-1}b\). Working out this product explicitly, we find:

\[
\Sigma(E) = - \sum_j \frac{H_{0j}^2}{E_j - E} = - \sum_j \frac{\omega_j^2}{E_j - E^2}.
\]

The only difference between this formula and equation (23) is the use of the exact (corrected) energy \( E \) in place of \( E_0 \). Equation (31) is the second-order Brillouin–Wigner perturbation theory [48–50] correction. Since \( E \) is not initially known, iterations are necessary to compute the final value. However, contrary to its ENPT counterpart, equation (23), the Brillouin–Wigner correction is not susceptible to divergence due to vanishing denominators. In this regard it is a competitor to the diagonal unitary correction, equation (25).

### 2.6. Perturbative generators’ ranking and improved optimization

Corrections introduced in section 2.4 provide an alternative (perturbative) rankings for the iQCC procedure. Namely, one can rank generators by their first-order ENPT contribution to the wavefunction [cf. equation (14)],

\[
|d_{ij}^{(1)}_{\text{ENPT}}| = \frac{2\omega_j |D_j|}{|D_j|},
\]

the exact location of the energy minimum in the unitary theory [see the derivation of equation (A3)]

\[
|\tau_j| = \arcsin \frac{2\omega_j}{\sqrt{D_j^2 + 4\omega_j^2}}.
\]

or the second-order ENPT absolute energy increments

\[
|\Delta E_{Ej}^{(2)}_{\text{ENPT}}| = \frac{\omega_j^2 |D_j|}{|D_j|}.
\]

Equations (32) and (33) are preferred in the case of strong correlation, in which small energy changes are accompanied by large amplitude variations, to select generators that change the wave function the most. Since the transition between weak and strong correlation regimes can be smooth to finally gauge which ranking is preferable the numerical testing is required. We perform such comparison in the subsequent sections.

Equation (33) also improves the efficiency of amplitude optimization. Namely, \( \tau_j \) is the value of the \( j \)th amplitude at the minimum of energy if couplings with other generators are neglected. For a single-generator QCC ansatz this result is exact and no further optimization is necessary. For multiple generators, \( \tau_j \) computed by equation (33) are usually a very good guess for the minimum. We observed approximately 30% savings in the number of calls to the gradient evaluation procedure for \( \geq 4 \) generators if the initial guess is computed by equation (33).

### 2.7. Active-space treatment in iQCC

iQCC is a variational method, which is equally capable of handling cases of weak and strong correlation. However, the canonical transformation step (6) invariably leads to the expansion of intermediate Hamiltonians. It is important, therefore, to carefully control which generators are included into the QCC ansatz (5). One way is to employ alternative ranking schemes, like those suggested in section 2.6. A more direct approach is to divide qubit indices into active and inactive sets. The active indices are assigned to a subsystem with strong mixing (entanglement), while the remaining ones are spectators which can be treated approximately. The most straightforward implementation of the idea can be made using the Jordan–Wigner fermion-to-qubit mapping, as in this case there is one-to-one correspondence between spin-orbitals and qubit indices, so that the traditional complete active space self-consistent field (CASSCF) treatment [1] will provide the guidance how to select the active qubit indices. Generators whose qubit indices are fully within the active set can be called internal; only such generators are included into the QCC ansatz. The other, external generators can be handled by perturbative/variational corrections introduced above. The construction can be made even more versatile by including semi-internal generators with a predefined number (1, 2, or more) of inactive indices into the QCC form. These semi-internal operators account for
partial relaxation of the environmental (external) degrees of freedom. However, generators whose indices
are fully external will never be treated exactly making the whole approach approximate.

3. Implementation

All the corrections developed above can be easily integrated into the iQCC workflow shown in figure 1. Once amplitudes are optimized by a classical computer using the energy values sampled by a quantum computer (‘the VQE-style optimization’) the Hamiltonian is dressed by equation (6) employing the optimized amplitudes on a classical computer. For the dressed Hamiltonian, its DIS is computed, and if the corrections are requested, the excited mean-field energies are evaluated by equation (22). Two out of three perturbative corrections can be computed immediately by equations (23) and (25) with negligible cost. The Brillouin–Wigner correction (equation (31)) requires an additional self-consistent procedure, whose cost is still small compared to the gradient computations. The variational-perturbative correction with the effective Hamiltonian of the dimension \( m > 1 \) (where \( N \) is the number of groups in the DIS) requires calculation of \( (m-1)(m-2)/2 + (m-1)(N+1-m) \) extra matrix elements of the matrix \( H \) (see equation (21)) plus multiple diagonalizations of \( h_{\text{eff}} \) (see equation (29)) to reach self-consistency.

Generators are ranked based on the absolute values of gradients (the original iQCC prescription) or using the measure (33). At this step the active-space treatment can be engaged by requiring that generators must belong to the active space. If the maximum gradient associated with chosen generators is below the convergence threshold, the iQCC procedure stops, otherwise a new iteration is started.

4. Results and discussion

All the numeric results reported here are obtained classically. The quantum part of the iQCC algorithm, namely, the optimization of amplitudes in the QCC ansatz at each iQCC iteration is performed on a classical computer. We set aside, therefore, any problems with noisy optimization of amplitudes; however, the whole iQCC scheme does not rely on the precise optimization of them. Even if only slightly improved (lower) energies are obtained, the procedure can move forward albeit at reduced efficiency. Dressing, building the DIS, (re)computing of the iQCC energies and corrections are invariably made on a classical computer. Thus, the quantum device is to be used as a quantum accelerator, much like how the graphical processing units (GPUs) are currently used to speed up certain steps of electronic structure calculations [51].

First we investigate one of the fundamental properties of any electronic structure method—the size consistency. The size consistency implies the correct (linear) scaling of energies when multiple non-interacting subsystems are considered. The iQCC method itself is size-consistent. It is known, however, that neither the linear variational method, nor the Epstein–Nesbet or the Brillouin–Wigner perturbation theories are size-consistent [52]. We expect, therefore, the lack of size consistency for our corrections too. This anticipated flaw, however, is not severe since the corrections to the iQCC energies (and hence the size-consistency error) can be made arbitrarily small at expense of additional iterations.

On the 10-qubit example of N\(_2\) dissociation we assess the ability of the corrections to reduce the number of iQCC iterations for the same target accuracy in both weakly and strongly correlated regimes. The 24-qubit symmetric water molecule stretching problem illustrates the active-space treatment and, finally, the large (56-qubit) problem of a single-triplet gap in Ir(ppy)\(_3\) demonstrates the scalability of the corrected iQCC method.

4.1. Size-consistency test: a non-interacting (H\(_2\))\(_2\)

We consider the non-interacting hydrogen molecule dimer (H\(_2\))\(_2\) in a planar rectangular geometry, in which the individual H\(_2\) moieties with R(H–H) = 0.75 Å are 100 Å far apart. The electronic Hamiltonians in the minimal STO-6G basis set are mapped by the JW transformation to 4- and 8-qubit operators for H\(_2\) and (H\(_2\))\(_2\), respectively. As was noted above, the JW mapping allows for exceptionally simple interpretation of a qubit mean-field wavefunction: each occupied spin-orbital is mapped to a \(|-1\rangle\) state of the corresponding qubit.

Pauli words and coefficients in equation (2) depend also on a molecular orbital (MO) set. For an H\(_2\) the natural choice is the set of the canonical Hartree–Fock orbitals; in this case the resulting 4-qubit Hamiltonian has only two terms in equation (9):

\[
\hat{H}(H_2) = \hat{I}_0(z) + I_{15}(z) \hat{x}_3 \hat{x}_2 \hat{x}_1 \hat{x}_0,
\] (35)
that is, the DIS has only one group. The qubit operator $\hat{x}_3 \hat{x}_2 \hat{x}_1 \hat{x}_0$ acting on the product state $|0\rangle = |−1\rangle_0 |−1\rangle_1 |+1\rangle_2 |+1\rangle_3$ maps it to the state $|+1\rangle_0 |+1\rangle_1 |−1\rangle_2 |−1\rangle_3$; in other words, it is a double-excitation operator. Mixing the doubly-excited configuration with $|0\rangle$ defines the FCI problem for a singlet state in this minimal basis set. The iQCC method converges at the second iteration after a single dressing of the initial Hamiltonian $H$ with $\exp(-i\tau \hat{x}_3 \hat{x}_2 \hat{x}_1 \hat{y}_0)/2)$. Since the iQCC procedure may take several iterations to converge for the dimer, to make a fair comparison, we report the iQCC energies and their corrected values (by equations (23), (25) and (31)) after the first iteration. Thus, the corrections are applied directly to the Hartree–Fock state.

There are several choices of MO sets for the dimer. The natural one is the canonical, fully delocalized and symmetry-adapted Hartree–Fock MOs. Alternatively, one can consider a set of localized orbitals which

Figure 1. Principal iQCC workflow.
stretched, the efficiency of corrections deteriorates. This result is not unexpected since the perturbative treatment is inefficient in the strongly-correlated regime. Nevertheless, the practical utility of the fragment-local orbital set corrections is still warranted as many experimental quantities, such as vibrational frequencies, etc refer to near-equilibrium configurations.

Table 1. Ground-state electronic energies (in $E_h$) for the non-interacting hydrogen molecule dimer, $(H_2)_2$, and their deviations from the corresponding doubled monomer energies in different approximation using various MO sets. The iQCC energy is for the first iteration, where it equals to the average value of $\hat{H}$ on the qubit product state, $|\psi\rangle$. The second-order Epstein–Nesbet (EN2), the diagonal unitary (DUC), and the Brillouin–Wigner (BW) corrections are computed by equations (23), (25), and (31) respectively.

| Molecular orbital set       | Total energy       | Deviation, $E[(H_2)_2] - 2E[H_2]$ |
|----------------------------|--------------------|-----------------------------------|
|                            | iQCC               | +EN2                              | +DUC                              | +BW                               |
|                            | iQCC               | +EN2                              | +DUC                              | +BW                               |
| Canonical Hartree–Fock     | −2.249 461 4989    | −2.282 452 1803                   | −2.282 384 7513                   | −2.281 927 6242                   | < $10^{-9}$                      | 9.6 $\times$ 10^{-3} | 9.1 $\times$ 10^{-3} | 9.6 $\times$ 10^{-3} |
| Fragment Hartree–Fock      | −2.249 461 4989    | −2.292 050 5739                   | −2.291 483 3452                   | −2.290 944 9976                   | < $10^{-9}$                      | < $10^{-9}$                   | < $10^{-9}$                   | 5.4 $\times$ 10^{-4} |
| Canonical Hartree–Fock      | −1.124 730 7495    | −1.146 025 2869                   | −1.145 741 6726                   | −1.145 741 6726                   | a The exact FCI value.             |

are sums of Hartree–Fock orbitals of $H_2$ fragments. Since there is no interaction between very distant fragments, the initial energy for both sets, $E^{(1)}_{\text{iQCC}} = \langle \emptyset | \hat{H} | \emptyset \rangle$ is identical; see table 1.

From table 1 it is clear that all corrections, as expected, are not size-consistent. The ENPT2 and DUC forms [equations (23) and (25)], but not the Brillouin–Wigner [equation (31)] one become size-consistent in the basis of fragment-local orbitals. On the other hand, the diagonal unitary correction and the Brillouin–Wigner formulas are exact for the two-level problem. Since the DUC and BW corrections are also not prone to divergence due to small denominators, they should be preferred over the ENPT2 one.

4.2. $N_2$ dissociation

The main goal of all corrections is boosting the computational efficiency of the iQCC method without sacrificing accuracy. Since both pristine and corrected iQCC energies ultimately converge to the exact answer, an important characteristics is the number of iterations that could be saved by applying corrections when a certain accuracy threshold is targeted, for example, 0.1 m$E_h$. To cover cases of weak and strong correlation we consider the $N_2$ dissociation curve using the minimal 6-electron/6-orbital complete active space, CAS(6,6), which allows for the correct dissociation of triply-bonded systems. In the beginning, the canonical Hartree–Fock MOs expanded in the correlation-consistent double-zeta Dunning basis set (cc-pVDZ) [54] were generated for each internuclear distance, and one- and two-electron integrals were transformed to this MO basis by the modified gamess program [55, 56]. The resulting second-quantized electronic Hamiltonian was converted to a qubit form using the parity transformation [57]. The advantage of the parity transformation used here is the presence of two stationary qubits that can be removed; as a result, a 10-qubit effective Hamiltonian containing the lowest singlet state of $N_2$ at all geometries can be constructed. The size of the problem, therefore, is small enough to carry out iQCC calculations with arbitrary accuracy.

The iQCC calculations were organized as follows. At every iteration 4 generators with the largest EN1 contributions (equation (32)) were selected for the use in the QCC ansatz (5) at the next one. Iterations were continued until the absolute maximum gradient of the generators from the DIS [equation (18)] decreased to 0.001, which translates into $10^{-3} - 10^{-6}$ Hartree of accuracy in total energies. Alternatively, the generators from the DIS were ranked according to their absolute gradient values, as in the original iQCC method. Note that the convergence criterion was chosen to be independent on the ranking formula because different ranking quantities have different physical dimensionality.

Figure 2 shows the number of iterations that are necessary to reduce the energy discrepancy $|E - E_{\text{FCI}}|$ below 0.1 m$E_h$. It is remarkable that at the chosen level of accuracy all corrections require the same number of iterations. Near the equilibrium geometry, $d(N - N) \approx 1.1 \text{Å}$, the corrections reduce the number of iterations by approximately a factor of 2 (e.g. at $d(N - N) = 1.0 \text{Å}$ from 13 to 6). As the molecule is stretched, the efficiency of corrections deteriorates. This result is not unexpected since the perturbative treatment is inefficient in the strongly-correlated regime. Nevertheless, the practical utility of the corrections is still warranted as many experimental quantities, such as vibrational frequencies, etc refer to near-equilibrium configurations.

We also assessed the EN-based generator ranking procedure (equation (32)); see figure 3. As anticipated, the EN-based ranking is better than the original, gradient-based one, albeit marginally. Thus, we recommend the use of the former for highly stretched molecules or in other cases of strong correlation. Ranking by (equation (32)) has a negligible computational cost as the weights are free by-products of the energy corrections.
4.3. Active-space treatment: the symmetric stretch of H$_2$O

A symmetric water molecule stretch is another archetypal type of a strong correlation problem. We consider a water molecule with fixed $\angle$HOH = 107.6°. When the 6-31G basis set is used and 1s core orbital of an O atom is frozen, the electronic Hamiltonian can be mapped to a 24-qubit operator. The size of the Hilbert space is $2^{24} \approx 1.7 \times 10^7$, which makes the straightforward iQCC calculations difficult. We partition 24 qubits into two sets: the 8-qubit active one and the inactive set containing the remaining qubits. We employed the JW fermion-to-qubit transformation, in which it is easy to link the active qubit set with the fermionic (4,4) complete active space (CAS). CAS(4,4) consists of two pairs of orbitals which correlate at the dissociation limit [58]. During QCC iterations only the generators with all-active indexes were ranked; four of them were included in the QCC ansatz for the next iteration. The convergence criterion was the same as for N$_2$: the procedure was stopped when the absolute maximum gradient in the active set fell below 0.001.

The resulting potential energy curves for the active-space iQCC method and its corrected counterparts are shown in figure 4. As can be seen, all the corrections to the iQCC energies are large even at convergence, which is a hallmark of the approximate nature of the bare active-space iQCC energies. The mean deviations from the exact curve decrease from approximately 117 mEh for the iQCC curve to 2.1 mEh and 5.8 mEh for DUC (equation (25)) and BW (equation (31)) corrections, respectively; see also table 2. While small mean deviations are important for some quantities, such as singlet-triplet gaps, it is equally important to have curves that are almost parallel to the exact one, to predict properties like equilibrium geometries or vibrational frequencies, correctly. All the corrections decrease the non-parallelity (the difference between maximum and minimum deviations, see table 2) for the whole considered region of O–H distances, from 0.75 to 2.65 Å. Moreover, both corrections drastically reduce the non-parallelity error for the region near...
Figure 4. Potential energy curves for the symmetric H₂O molecule stretch. The active-space qubit treatment, equivalent to CAS(4,4) embedded into the FCI ('exact') problem (the Hartree–Fock orbital, which correlates with the 1s orbital of O is frozen) in the 6-31G basis. The numbers beside points are the number of terms in dressed Hamiltonians at convergence; the initial number of terms is 9.2 × 10³.

Table 2. Various integral characteristics of curves in figure 4. All quantities are in mEh.

| Method     | Deviation, (E – E_{exact}) |
|------------|-----------------------------|
|            | Max | Min | Average | Non-parallelity |
| iQCC       | 133 | 99  | 116     | 33              |
| iQCC + DUC | 16  | −12 | 2       | 29              |
| iQCC + BW  | 18  | −7  | 5       | 26              |

the equilibrium geometry, 0.85 ≤ d(O–H) ≤ 1.15 Å: from 15 mEh to 4–5 mEh. This result is consistent with the expectation that the perturbation theory-based corrections are more reliable when correlation is not too strong.

4.4. T1–S0 gap in the Ir(ppy)₃ complex

Encouraged by performance of the perturbative corrections near equilibrium configurations, we applied the enhanced iQCC method to a large, technologically relevant system, the tris-(2-phenylpyridine)iridium(III), Ir(ppy)₃ complex; see figure 5. This molecule is probably the most studied green phosphorescent emitter [59–62] widely used in organic light-emitting diodes (OLEDs) [63]. Excited by recombination of electrons and holes injected from the corresponding transport layers, Ir(ppy)₃ emits predominantly from the lowest triplet state (the singlet state is also bright) with almost 100% quantum efficiency. For the targeted design of similar and more advanced emitters it is important to reliably predict singlet-triplet gaps (in either singlet and triplet equilibrium geometries), but due to the size of molecules, the electronic-structure studies are typically limited to the density-functional theory (DFT) [64–66], with a prominent counterexample [67].

The ground singlet electronic state Ir(ppy)₃ is reasonably well described by single-determinant Hartree–Fock or DFT methods. On the contrary, the triplet state is strongly multi-configurational with a multitude of closely-spaced energy levels that arise from population of low-lying d-orbitals of the Ir atom by an unpaired electron and its delocalization across the conjugated system. If the unrestricted Hartree–Fock method is used to describe the triplet state, the value of \( \langle \hat{S}^2 \rangle \) is approximately 5, deviating markedly from the ideal value of 2. Thus, the correct electronic structure is likely to be determined by a balance of orbital mixing and correlation effects, so that the CASSCF method may be the best choice for the problem; however, capturing dynamical correlation typically requires unrealistically large active spaces [68].

To calculate the singlet-triplet gap we have first optimized the molecular structure of mer – 3Ir(ppy)₃ using the restricted open-shell Hartree–Fock (ROHF) method, which guarantees the spin purity of a Slater determinant. For the Ir atom we employed the 60-electron relativistic effective core pseudopotential (RECP) [69] with a partner double-zeta valence basis set as implemented in GAMESS, and the Pople split-valence double-zeta basis set augmented with polarization d orbitals for the second-row atoms C and N, 6-31G(d).

With six-component d harmonics the atomic basis for the molecule contained 622 functions. After the equilibrium geometry has been located, CAS(26e, 28o) has been created using 13 occupied and 15 unoccupied Hartree–Fock orbitals below and above the Fermi level, respectively. The electronic Hamiltonian corresponding to that CAS was generated and converted into the 56-qubit operator using the
Table 3. Various estimates for the singlet-triplet gap for Ir(ppy)$_3$.

| Method                   | Singlet-triplet gap$^*$ | nm   |
|--------------------------|-------------------------|------|
| ΔSCF(HF)                 | 2.95                    | 421  |
| ΔSCF(DFT/B3LYP$^*$)      | 2.26                    | 549  |
| ΔMP2                     | 2.58                    | 481  |
| iQCC(1 iter)             | 2.57                    | 483  |
| iQCC(1 iter) + DUC       | 2.59                    | 485  |
| iQCC(5 iter)             | 2.56                    | 485  |
| iQCC(10 iter)            | 2.98                    | 416  |
| iQCC(10 iter) + DUC      | 2.54                    | 488  |
| Exp.$^c$                 | 2.52                    | 491  |

$^*$In the triplet geometry optimized at the restricted open-shell Hartree–Fock level.

$^b$References [70] and [71].

$^c$In $\sim 10^{-5}$ M solution in 2-MeTHF at 77 K; see reference [72].

JW mapping and a pairwise grouping ($1\alpha, 1\beta, 2\alpha$, etc) of spin-orbitals; the resulting Hamiltonian [equation (2)] contained 901985 terms. A similar procedure was carried out for the singlet state in the same geometry: first, the restricted Hartree–Fock MOs were generated, then CAS(26e, 28o) was selected, and finally, the 56-qubit Hamiltonian was assembled from the values of one- and two-electron integrals in the chosen MO basis using the JW transformation resulting in 901973-term operator.

We were able to perform 10 iQCC iterations using a single-generator QCC ansatz (5), results are shown in table 3. We compare the iQCC method with and without corrections against the low-scaling DFT and MP2 methods as well as the experimental values, since straightforward CASSCF calculations are not possible for the chosen size of CAS. We leave more comprehensive assessment to future studies.

It appears that the most of the correction to the ΔSCF can be captured perturbatively, as both ΔMP2 and 'iQCC(1 iter) + DUC' results are already quite close to the reference value. The bare iQCC estimates behave non-monotonically, which is explained by slightly different rates of convergence of the absolute iQCC energies for singlet and triplet states. Corrected iQCC values ('+DUC'), however, exhibit the monotonic convergence. Overall, the iQCC procedure converges slowly, and without perturbative corrections such a situation is detrimental for the iQCC method, as one would need to carry out prohibitively many iterations to reach the desired accuracy.
5. Conclusions

We have developed and tested several numerical techniques that are aimed to \textit{a posteriori} correct energies computed by the iQCC method. They are rooted in a new representation for qubit Hamiltonians, equation (9), in which regular and simple rules exist for evaluating matrix elements with the direct-product qubit states, equations (11) and (12). In this respect it has a lot in common with normal-ordered fermionic Hamiltonians. The new decomposition naturally leads to a linear variational ansatz (19). Being not suitable for quantum computers, it allowed us to formulate the CI-like variational problem (20) and the qubit form of the second-order Epstein–Nesbet perturbation theory, equation (23); both can be efficiently evaluated on a classical computer.

Two essential modifications for the aforementioned techniques were also developed. The first is aimed to circumvent the divergence of the ENPT series due to small denominators in the strong correlation regime [see Equation (25)]. The second is the unified variational-perturbational scheme, which ‘interpolates’ between purely variational and perturbative solutions (see section 2.5) for flexible control of computational efforts. The unified scheme in the limit of a trivial $1 \times 1$ effective Hamiltonian matrix reduces to the second-order Brillouin–Wigner perturbation theory.

Evaluation of the perturbative corrections requires only the mean-field excited energies [equation (22)], everything else is available as a part of the original iQCC procedure. The computational overhead is strictly linear in the size of the dressed Hamiltonian and small even for the largest 56-qubit problem considered in this work.

By capturing some of energy contributions classically, we further decrease the use of quantum resources. First of all, the total number of iQCC iterations is decreased for the same accuracy requirements. Secondly, by limiting the qubit indices of generators to be in the active set, we limit the growth of intermediate Hamiltonians and, thus, the number of quantum measurements needed at subsequent iterations.

Numerical assessment of the proposed techniques on several prototypical problems, namely, 10-qubit $N_2$ dissociation, the 24-qubit symmetric water molecule stretch, and finally, and large-scale, 56-qubit simulations of the singlet–triplet gap in the Ir(ppy)$_3$ complex have demonstrated a substantial improvement over the original iQCC method. New corrections address the most severe shortcoming of the original iQCC method: its numerical inefficiency in the case of weak correlation; they also provide additional flexibility in cases when only a subset of qubits is strongly correlated.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Appendix A. Diagonal unitary (infinite-order) modification of the ENPT2 correction

The ENPT expression (23) diverges as $D_j \to 0$. The problem can be mitigated by modifying the denominators, and a variety of strategies were suggested in literature [73, 74], but here we derive a \textit{degeneracy-corrected} formula, which was first suggested in reference [46] as a modification to the second-order Moller–Plesset energy expression. Later on, similar formulas were used in the context of iterative CI methods [29, 43].

Consider a qubit Hamiltonian with only one $X$ term, $\hat{I}_k(z)\hat{X}_k$, in equation (9). This is the case, for example, of the $H_2$ molecule in the minimal basis. It is easy to show that a single-generator QCC ansatz with $\hat{P}_k = \hat{X}_k \hat{Z}_j$, where $j$ is an arbitrary number from 1 to $2^n$ having the odd-number bit overlap with $k$, finds the exact ground state. Indeed, the variational expression for the energy is:

$$E(\tau) = \langle 0 | e^{i\tau \hat{H}_{2}/\hbar e^{-i\hat{H}_{1}/2}} | 0 \rangle$$

$$= E_0 + \left\langle 0 \left| \left( \frac{1}{2i} \right) [\hat{H}, \hat{P}_k] \right| 0 \right\rangle \sin \tau$$

$$+ \left\langle 0 \left| \frac{1}{2} \left( \hat{P}_k \hat{H} \hat{P}_k - \hat{H} \right) \right| 0 \right\rangle (1 - \cos \tau), \quad (A1)$$
where $E_0 = \langle 0 | H | 0 \rangle$. Identifying $\omega_k = |D_k|/2E_k$ and $D_k = \langle 0 | P_k H P_k - H | 0 \rangle = E_k - E_0$ we can write

$$E(\tau) = E_0 + \omega_k \sin \tau + \frac{D_k}{2} (1 - \cos \tau). \tag{A2}$$

Combining all trigonometric functions together we find that

$$E(\tau) = E_0 + \frac{D_k}{2} - \sqrt{\left(\frac{D_k}{2}\right)^2 + \omega_k^2} \cos (\tau + \phi_k), \tag{A3}$$

where $\phi_k = \arcsin \frac{2 \omega_k}{\sqrt{D_k^2 + \omega_k^2}}$. The minimum of the equation (A3) corresponds to $\cos(t + \phi_k) = 1$, and the energy correction is:

$$E_{\text{corr}} = E_0 - \frac{D_k}{2} - \sqrt{\left(\frac{D_k}{2}\right)^2 + \omega_k^2}. \tag{A4}$$

It is clear that $\omega_k^2$ and $D_k$ are the numerator and the denominator of one particular term in equation (23). Thus, assuming independent (fully uncorrelated) contribution of every generator $P_k$ we arrive to equation (25).

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