Reducing Qubit Requirements while Maintaining Numerical Precision for the Variational Quantum Eigensolver: A Basis-Set-Free Approach

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We present a basis-set-free approach to the variational quantum eigensolver using an adaptive representation of the spatial part of molecular wavefunctions. Our approach directly determines system-specific representations of qubit Hamiltonians while fully omitting globally defined basis sets. In this work, we use directly determined pair-natural orbitals on the level of second-order perturbation theory. This results in compact qubit Hamiltonians with high numerical accuracy. We demonstrate initial applications with compact Hamiltonians on up to 22 qubits where conventional representation would for the same systems require 40-100 or more qubits. We further demonstrate reductions in the quantum circuits through the structure of the pair-natural orbitals.

Within the framework of the Born–Oppenheimer approximation, the electronic structure of molecules is described as a multi-dimensional wave function of electrons in an external potential, usually generated by the charges of the nuclear framework. Finding accurate approximations to describe those multi-dimensional wave functions is one of the key goals in quantum chemistry, and several types of models have emerged over the last decades. [1] Most models formally decompose the multi-dimensional electronic wave function into a linear combination of anti-symmetrized tensor products (Slater determinants) of one-electron wavefunctions (spin-orbitals). The spin component can be described completely by the two spin-up and spin-down basis states, leaving only the spatial part of the orbitals to be represented. Traditional electronic structure packages usually use global sets of atom-centered basis functions to describe the spatial parts of the orbitals. Those basis functions mimic the solutions of the Hydrogen atom and the whole procedure is referred to as a linear combination of atomic orbitals (LCAO). The by far most prominent choice are atom-centered Gaussian functions multiplied by polynomial factors. [2, 3] The exponents of the Gaussian functions are globally defined for each atom which leads to a large number of individual basis sets (the EMSL basis set exchange library [4] lists currently 429 different basis sets for the carbon atom alone), making it a non-trivial task to pick the right basis set for the right computation. Alternatives to Gaussian basis sets, such as exponential functions [5] (Slater-type basis sets) and Sturmians [6], exist and are topic of ongoing research, but are still relying on globally defined basis sets. Basis-set-free approaches represent the spatial part of the orbitals or other wavefunctions without the use of a globally defined basis set. Some examples are approaches based on Daubechies wavelets [7–9], Lagrange-sinc functions [10] or multi-resolution analysis (MRA) [11–14]. MRA offers an alternative to the traditional basis sets by representing the spatial parts of molecular wavefunctions on adaptive real-space grids, where wavelet-based numerical techniques allow adaptive refinement of the grid in a black-box fashion. In this representation each function (orbital) is described individually by automatically constructed adaptive multi-waves being each a basis-set-free representation, since the numerical basis is individually constructed from a proper $L^2$ basis with a numerically well defined truncation criterion. MRA allowed the development of highly accurate quantum chemistry algorithms for ground-state energies [11, 15], excitation energies [16, 17], polarizabilities [18, 19], magnetic properties [20, 21], as well as relativistic applications [22, 23] using multi-field and density functional theory (DFT) models. Initial treatment of correlated methods beyond density functional theory aimed at representing multi-electron wavefunctions directly, resulting in basis-set-free and virtual-orbital-free approaches. [24–27] Recently, an approach to directly determine MRA-represented pair natural orbitals (MRA-PNOs) on the level of Møller-Plesset perturbation theory of second order (MP2) was demonstrated. This approach allows to grow near-optimal system-adapted PNOs from scratch, omitting the use of global basis sets completely. In this work, we will apply those MRA-PNOs in a more general framework beyond the MP2 model, similar to PNO-based methods within LCAO approaches. [28–31]

Classical quantum chemistry algorithms are highly optimized towards Gaussian basis sets (GBS), which makes them the dominant choice of representation. Quantum algorithms have not reached this highly optimized stage.
and current research is exploring alternative representations, for example plane-waves [32] or Gausslets [33], which offer advantages over Gaussian basis sets within the context of quantum computation. In this work, we introduce a basis-set-free approach to the variational quantum eigensolver (VQE) [34, 35], a class of algorithms that variationally minimize the expectation value of a qubit Hamiltonian using a parametrized quantum circuit. The basis-set-free qubit Hamiltonians are constructed from directly determined occupied Hartree–Fock orbitals and MRA-PNOs. [36] In contrast to global basis sets, the orbitals are optimized system-specific with a surrogate model (MP2), that already accounts for electron correlation. This allows for the construction of compact qubit Hamiltonians, that require a significantly lower number of qubits compared to their LCAO based counterparts. In variational quantum algorithms, the reduction of the qubit resources has become one of the main objectives, particularly for applications in chemistry. Recent approaches include external corrections, such as the (virtual) quantum subspace expansion [37] or explicitly correlated approaches in the form of trans-correlated Hamiltonians [38, 39], and often come with additional costs in quantum measurements and classical computation. These methods can as well be applied within the framework of this work and potentially lower the qubit resources even further. Here, we develop a way to directly construct system-specific compact qubit Hamiltonians with high numerical precision providing a path towards high accuracy quantum chemistry with variational quantum algorithms.

I. METHODOLOGY

When solving the electronic structure problem, one aims to find approximations for the eigenenergies of electronic Hamiltonians, which for \( N_e \) electrons with coordinates \( \vec{r}_k \in \mathbb{R}^3 \) are defined as

\[
H (\vec{r}_1, \ldots, \vec{r}_{N_e}) = \sum_{k=1}^{N_e} h (\vec{r}_k) + \frac{1}{2} \sum_{k \neq l} g (\vec{r}_k, \vec{r}_l),
\]

where \( h = T + V \) denotes the one-electron kinetic energy operator \( T \) with the external potential \( V \), and \( g (\vec{r}_k, \vec{r}_l) \) the electron-electron Coulomb potential. For molecules, the external potential \( V (\vec{r}) \) is given by the sum of Coulomb potentials between the individual point charges of the nuclei and an electron at position \( \vec{r} \). The eigenfunctions of the electronic Hamiltonian are anti-symmetric, multi-dimensional functions in \( \mathbb{R}^{3N_e} \), making brute-force grid-based computation an unfeasible task. The requirement of having an anti-symmetrized wavefunction arises from the fermionic nature of the electrons and is usually handled by using Slater determinants or anti-commuting second-quantized operators.

In order to tackle this challenge, a large family of approximations to the electronic wavefunction have been introduced. The most prominent is the Hartree–Fock (HF) method, that variationally optimizes a single Slater determinant, therefore reducing the \( 3N_e \)-dimensional problem to \( N_e \) coupled, three-dimensional, non-linear problems. Improvements upon Hartree–Fock, like configuration-interaction (CI) and coupled-cluster (CC) methods, add more anti-symmetrized functions to the wavefunction ansatz, usually created by replacing \( n \) orbitals in the initial determinant by correlated \( n \)-electron functions. In conventional quantum chemistry, the spatial parts of the Hartree–Fock orbitals are represented with globally defined fixed LCAO basis sets for each individual atom. The Hartree–Fock algorithm is then simplified to optimize only the LCAO coefficients, resulting in the Roothaan equations, which often are still referred to as Hartree–Fock. A \( N \)-orbital basis set results in \( 2N \)-orthonormal spin-orbitals, of which the first \( N_e \) define the Hartree–Fock reference determinant. This leaves \( 2N-N_e \) virtual spin-orbitals free to represent the correlated electron functions used in CI and CC methods. [26]

Within the language of second quantization, the description of these methods can be significantly simplified, [3, 40–42] by expressing the electronic Hamiltonian with abstract field operators [43] \( \hat{\psi} (x) \), \( \hat{\psi}^\dagger (x) \), that create or annihilate electron density at spin-coordinate \( x = (\vec{r}, \sigma) \)

\[
H = \int \, \! dx \, \hat{\psi}^\dagger (x) \bigl[ h (x) \bigl( \hat{\psi} (x) \bigr) + \frac{1}{2} \int \, \! dy \, \hat{\psi}^\dagger (x) \bigl( \hat{\psi}^\dagger (y) g (x, y) \bigl( \hat{\psi} (y) \bigr) \bigl( \hat{\psi} (x) \bigr) \bigr) \bigr] \, \! dx.
\]

Formal expansion of the field operators into an orthogonal set of spin-orbitals as \( \psi (x) = \sum_k \varphi_k (x) a_k \) leads to the numerically more suitable form

\[
H = \sum_{kl} h_{kl} \hat{a}^\dagger_k \hat{a}_l + \frac{1}{2} \sum_{klmn} g_{klmn} \hat{a}^\dagger_k \hat{a}^\dagger_l \hat{a}_m \hat{a}_n,
\]

were \( h_{kl} \) and \( g_{klmn} \) are integrals over spin-orbitals in Dirac notation. Within the scope of variational quantum algorithms, the second-quantized Hamiltonian can then be transformed to a qubit Hamiltonian using various encodings [44–46]. Canonically, when global basis sets are used, the second-quantized Hamiltonian in Eq. (3) is constructed by the occupied and virtual Hartree–Fock orbitals. This can be interpreted as pre-optimizing the orbitals within a fixed set of basis functions by a mean-field method. In this work, we construct the second-quantized Hamiltonian from the occupied Hartree–Fock orbitals, solved variationally within a multiresolution analysis representation, [11] combined with directly determined pair-natural orbitals, [36] optimized by MP2. In other words, we are pre-optimizing the orbitals with a correlated method.
and within a basis-set-free adaptive representation. The orbitals represented by MRA are basis-set-free since they do not require a globally defined fixed set of basis functions but are instead individually represented by adaptively constructed sets of piecewise polynomials. [11–13] The construction of the multiresolution representation on a grid is carried out automatically, and for most applications, the user does not require detailed knowledge about the underlying machinery. Hence, from a user perspective, this representation can be treated as effectively basis-free and is sometimes referred to as just basis-free. To build a Hamiltonian, it is only necessary to set a numerical accuracy threshold (in this work, this is \( \epsilon = 10^{-4} \)) and the required number of orbitals. In Fig. 1, we illustrate the construction of the qubit Hamiltonians using the basis set and the MRA-PNO based basis-set-free approach. Conceptually, the biggest difference to the canonical construction is, that our approach does not rely on globally fixed sets, but rather optimizes the orbitals directly and system-specific. This allows the freedom to adapt to the molecule at hand, in order to find a close-to-optimal compact representation. In general, the underlying representation of the pair-natural orbitals can be chosen freely, and does not necessarily need to be MRA. If a sufficient large Gaussian basis-set is chosen, the PNO representation using this basis-set will lead to similar qubit Hamiltonians as obtained with MRA-PNOs. In other words, once computed, the large qubit Hamiltonians of Tab. I could be reduced to similar sizes as the qubit Hamiltonians constructed from MRA-PNOs - similar to Ref. 47 where such an approach is used with intrinsic atomic orbitals instead of pair natural orbitals. There is however no guarantee, that the chosen Gaussian basis-set is sufficient and picking the right basis-set for the right task depends widely on heuristics and trial and error procedures. We chose MRA-PNOs, since they are usually close to optimally represented pair-natural orbitals, allowing us to focus on the surrogate model itself, without having to speculate about basis-set effects. It was shown before, that the direct construction of pair natural orbitals in this way can reach accuracies beyond existing Gaussian basis sets within second-order methods. [36] Current implementations can run with molecular systems consisting of dozens of atoms, making it a realistic candidate for future large-scale applications.

A. Constructing the Hamiltonian:

Most MRA-based optimization protocols in quantum chemistry solve a quantum chemical model, defined by the potential \( V \), by transforming the Schrödinger-like differential equation

\[
\left( -\frac{\Delta}{2} + V \right) |\Psi\rangle = E |\Psi\rangle
\]

leading to an iterative optimization of the wavefunction. [48, 49] The potential \( V \) depends on the underlying quantum chemical model and is usually an effective one-body potential from Hartree–Fock and Kohn–Sham theory [11] with corresponding excited state vari- ants [16, 17], or an effective two-body potential from an integral equation using the bound-state Helmholtz Green’s function \( G_E \) as kernel

\[
\Psi (r) = -2 \int d r' G_E (r, r') V (r') \Psi (r'),
\]

and within a basis-set-free adaptive representation.
MP2 [24, 25] and Coupled-Cluster approaches [26, 27]. While more general many-body potentials are possible in theory [50], they are computationally challenging and have not been realized yet. In this work, the potential \( V \) is the PNO-MP2 Hylleraas potential, an effective one-body potential described in detail in Ref. 36. We refer to a recent review [13] for further details on MRA-based methods.

In this approach, occupied and localized Hartree–Fock orbitals are optimized according to Ref. 11, and initial pair-specific guess functions for the PNOs are created by multiplying monomials onto the optimized Hartree–Fock orbitals. These initial PNOs are optimized according to Eq. (5), where \( V \) is determined by the PNO-MP2 Hylleraas functional. [36] The optimization results in multiple sets of pair-natural orbitals corresponding to pairs of occupied Hartree–Fock orbitals \(|i\rangle\) and \(|j\rangle\)

$$ S_{ij} = \bigcup_{a_{ij}=1}^{r_{ij}} \{|a_{ij}\rangle\}, $$

where the ranks \( r_{ij} \) depend on the occupation numbers of the pair-natural orbitals, the truncation threshold, and the number of available initial guess functions. In this work, we used two cycles of guess function construction according to Ref. 36, and set the PNO ranks according to the desired number of qubits. In order to construct the qubit Hamiltonians, we first globally select the MRA-PNO-MP2 calculation, and a transformation of the orthonormalized PNOs, using Cholesky or other techniques can be performed directly in the MRA representation, requiring only the computation of the PNO overlaps, \( O \left( \left( \frac{N_e}{2} \right)^2 \right) \), already required within the MRA-PNO-MP2 calculation, and a transformation of the orbitals, \( O \left( \left( \frac{N_e}{2} \right)^3 \right) \), afterwards. The Hartree–Fock calculation within MRA formally scales quadratically with system size and has the potential to be further reduced. [13, 53]

### B. Constructing PNO-Specific Unitaries

Since the qubit Hamiltonians of this work are constructed by occupied Hartree–Fock orbitals and pair-natural orbitals given in Eq. 6, this additional structure can be exploited in the construction of the quantum circuit. The PNO-MP2 surrogate model itself contains only double excitations from occupied Hartree–Fock orbitals \(|i\rangle\), \(|j\rangle\) to the pair-specific PNOs \(|\tilde{a}_{ij}\rangle\), and this excitation structure can be transformed directly to construct unitary quantum circuits. In the case of pair-excitation models, such as the \( k \)-UpCCGSD model, we can define the PNO-restricted doubles and generalized doubles models as

$$ |\text{PNO-UpCCD} \rangle = U_D U_{HF} |0\rangle, $$

$$ |\text{PNO-UpCCGD} \rangle = U_{GD} U_D U_{HF} |0\rangle, $$

using the PNO-restricted unitary operators

$$ U_D = \prod_{i=1}^{N_e} \prod_{a \in S_{ia}} e^{-i \frac{\theta}{2} \tilde{G}_{iaia}} $$

$$ U_{GD} = \prod_{i=1}^{N_e} \prod_{a,b \in S_{ia,ib}} e^{-i \frac{\theta}{2} \tilde{G}_{abab}} $$

and the pair excitation generator defined as

$$ \tilde{G}_{iaia} = i \left( a_{ia}^\dagger a_{ia} a_{ia}^\dagger a_{ia}^\dagger - h.c. \right). $$

The incorporation of (generalized) singles can be realized in the same way, with the single excitation generators corresponding to the used double excitation
II. INITIAL APPLICATIONS

To evaluate the accuracy and efficiency of the proposed approach, we employ MRA-PNO-MP2 as a basis-set-free surrogate model to the variational eigen solver. We employed the UpCCGSD model of Ref. 56 to construct the quantum circuits. All used model systems are chosen such that they are well described by this ansatz, which allows to focus on the numerical accuracy of the qubit Hamiltonians without worrying about the quality of the ansatz. An overview of the qubit requirements using MRA and GBS representations is given in Tab. I, where we report significant improvement for all systems and types of energy metrics investigated in this work. As energy metrics we used non-parallelity (NPE) and maximum (MAX) errors on potential energy surfaces and a reaction barrier (ΔE).

VQE calculations are performed with TEQUILA [57] using qulacs [58] as quantum backend, the BFGS optimizer of scipy [59] and the qubit encodings of openfermion [60]. Analytical gradients for the BFGS optimization were obtained automatically through the techniques described in Ref. 61. LCAO reference calculations are performed with psi4 [62]. In all VQE calculations the parameters are initialized as zero - i.e. starting from the Hartree–Fock reference state. Representations of Hamiltonians are abbreviated with MRA(N_e,N_q) for MRA-PNOs and the acronym for standard LCAO basis sets. The values in parentheses represent the number of electrons N_e and qubits (spin-orbitals) N_q. Note, that classical FCI calculations with basis sets corresponding to large qubit Hamiltonians with 50 or more qubits are possible, since these algorithms are not operating in the full Fock space of the second quantized Hamiltonian. For simplicity, we omitted known general compression schemes that allow to reduce the number of qubits by two when combined with parity based encodings [63], since these would apply to all qubit Hamiltonians in this work in the same way. The numerical accuracy of the qubit Hamiltonian is independent of the encoding and the results of this work were obtained with the Jordan-Wigner representation, our implementation within TEQUILA however does support other encodings. The qubit encoding can influence the results of possible future demonstrations on real quantum hardware, since it will result in different gate decomposition of the VQE unitary and therefore will have varying properties with regard to the specifics of the device noise characteristics.

A. Helium and Beryllium Atom

As an initial test, we computed the energies of the Helium and Beryllium atom, where the true energies close to the complete basis set (CBS) limit are known from different highly accurate numerical calculations in the literature. [64–66] The results are shown in Fig. 2, where we show the absolute energies with respect to the qubit

| System Metric | MRA | GBS | More |
|---------------|-----|-----|------|
| He MAX       | 4   | 4-10| Fig. 2 |
| Be MAX       | 10  | 10-18| Fig. 2 |
| H₂ NPE       | 4   | 20-56| Figs. 6, 3 |
| H₂ NPE       | 8   | 20-56| Figs. 6, 3 |
| H₂ MAX       | 20  | 56-120| Figs. 6, 3 |
| H₂ MAX       | 8   | 8   | Figs. 6, 3 |
| H₂ MAX       | 20  | 56  | Figs. 6, 3 |
| LiH NPE      | 12-22| 38-88| Figs. 6, 3 |
| LiH MAX      | 12  | 38-88| Figs. 6, 3 |
| LiH MAX      | 22  | 170-288| Figs. 6, 3 |
| BH NPE       | 12-22| 38-88| Figs. 6, 3 |
| BH MAX       | 12-22| 38-88| Figs. 6, 3 |
| BeH₂ NPE     | 12  | 46-114| Figs. 6, 3 |
| BeH₂ MAX     | 12  | 24-46| Figs. 6, 3 |
| NH₃ ΔE       | 12-18| 58-100| Fig. 5 |
compared to

plained the significantly better performance of
ttracted basis function while the
STO-6G
for example uses three Gaussians to represent one con-
tacted Gaussian basis functions. The
functions. Gaussian basis sets mitigate this through con-
potential, and non-representable by primitive Gaussian
functions due to the singularities in the nuclear Coulomb
nuclear cusp
[67, 69] in the wavefunctions, generated
as a separated representation using one-electron
orbital. These techniques can already be
present in the initial guess functions for the MRA-PNOs.
So, this is also the case for the MRA-PNOs in this
work, since the many-electron wavefunction is still rep-
resented as a separated representation using one-electron
wavefunctions. For the Helium atom, a decrease in the
slope of the convergence can already be observed, and we
expect the same for the Beryllium atom with increasing
number of qubits. The basis-set-free approach however achieves significantly more accurate results compared to the
LCAO representations. In future works, the representation
could be further improved by explicitly correlated
approaches that correct the inaccurately description of the
electronic cusp. [66] These techniques can already be
applied in the MRA-PNO optimization [36], and recently
such methods have been introduced for VQEs in the form of
transcorrelated Hamiltonians. [38, 39]

B. Bond Dissociation Curves

We simulated VQE energies, employing UpCCGSD,
and the pair-specific PNO-UpCCD model, along the
potential energy surfaces of the small molecules H₂, LiH,
BH and BeH₂ and compared it with the best affordable
variational methods using the large Gaussian basis sets.
The potential energy surfaces are shown in Figs. 4 and 6.
Similar as for the Helium atom in Fig. 2 we show the
PNO-MP2/MRA results in Fig. 4 to illustrate that the
problem is not fully solved by the surrogate model which
performs poorly for the stretched geometries and the
improvements in the method are in this case within the
same range as the improvements in numerical representation.
For H₂ we furthermore show GBS calculations
where the basis set was optimized for each point indi-
vidually according to Ref. 70 using the DIFFQUET [72]
package. This can be seen as an intermediate approach
using Hartree–Fock as a surrogate model and allowing
the basis set to relax. In the (2,4) representation the
optimal spatial orbitals can be well approximated by
two atom-centered s-type orbitals, leading to significant
improvements in the optimized STO-3G representation
if individual optimization is enabled. For the slightly
larger 6-31G basis set, individual optimization does not
lead to improvements. In this case, the optimal (4,8)
spatial orbitals contain two π orbitals which intrinsically
can not be represented by the 6-31G basis set but
are well approximated by MRA where the techniques
of Refs. 16, 36 ensure that the correct symmetries are
present in the initial guess functions for the MRA-PNOs.

In order to accurately describe chemistry, obtaining con-
sistent relative energies over different molecular structures is in most cases more important than accurate ab-
solute energies. In Fig. 3, we use non-parallellity (NPE)
and maximum (MAX) errors as accuracy metrics with
the best achievable method and Gaussian basis set as
reference. We chose the three diatomic molecules here
such that UpCCGSD is a good ansatz, i.e. differences
to FCI are below the millihartree threshold for STO-3G
and 6-31G simulations. For the BeH₂ molecule, UpC-
CGSD did not always converge towards the best solu-
tion. We employed adaptive operator growth according
to Refs. 73 and 61, in order to reach the lowest ener-
gies of the given PNO Hamiltonians. As references, we
used FCI/cc-pVQZ(2,120) for H₂, FCI/cc-pCVQZ(2,288)
for LiH, CISD'TQ/cc-p CVTZ(6,114) for BH and FCI/cc-
pVQZ(4,224) for BeH₂. Comparison with accurate nu-
merical results from Refs. 71 and 65 confirms, that the
reference values for H₂ and LiH are close to the basis set
limit. In terms of NPE and MAX errors (Fig. 3), the
basis-set-free VQE clearly outperforms the traditional
basis sets with the same number of qubits as well as the
cc-pVQZ simulations, which use approximately twice the
number of qubits. The error of the MRA-PNO represen-
tation tends to grow with larger bond distances. This re-
sult is not unexpected, as the MP2 surrogate model per-
forms worst in this regime. The effect on the orbitals
determined by the surrogate model are however not that se-
vere. In contrast, the GBS representation performs best
at large bond distances. This is also not surprising, since
these basis sets are optimized for the atomic systems.

|     | A        | B        | C        |
|-----|----------|----------|----------|
| LiH(4,12) | 4 (192) | 12 (352) | 45 (1280) |
| BH(6,12) | 3 (144) | 9 (240)  | 45 (1280) |
| BeH₂(4,12) | 4 (192) | 12 (368) | 45 (1280) |
| LiH(4,22) | 9 (432) | 27 (1216)| 165 (6160)|
| BH(6,22) | 7 (336) | 21 (848) | 165 (6160)|
Figure 2. **Helium (A) and beryllium (B) atoms:** Classical full-CI energies compared with basis-set-free VQE energies for the Helium (A) and Beryllium (B) atoms. The VQE part uses the UpCCGSD ansatz. UpCCGSD results with small Gaussian basis sets are nearly indistinguishable from the FCI results and are omitted in the plots. The reference values FCI/CBS are $-2.9037$ [64–66] and $-14.667$ [65] in Hartree units.

Figure 3. **Non-parallelity (NPE) and maximum errors (MAX):** Comparison of NPE and MAX errors of the potential energy surfaces of Fig. 6 using standard Gaussian basis sets (GBS) or the basis-set-free VQE approach (MRA). The used reference values are FCI/cc-pVQZ(2,120) for $\text{H}_2$, FCI/cc-pCVQZ(4,228) for LiH, CISDTQ/cc-pCVTZ(6,114) for BH and FCI/cc-pVQZ(4,224) for $\text{BeH}_2$. The GBS for the VQE are STO-3G, 6-31G and cc-pVDZ.

The PNO-restricted unitaries perform well at not-too-far-stretched bond distances, where they offer significant savings in the number of operators used for the UCC ansatz (see Tab. II). This ansatz can be viewed as an even further restricted form of the approach in Refs. 54 and 74, where all configurations in the UCC wavefunction are restricted to double occupancies. In contrast to Ref. 54, the PNO-UpCCD ansatz however performs well for all bond distances of LiH. The reason for this lies in the PNO structure, that is not present in canonical Hartree–Fock orbitals. Note, that this is independent of the underlying numerical representation of the orbitals.

C. **Umbrella reaction of Ammonia**

As a last example, we simulate the umbrella reaction of ammonia, a small intra-molecular reaction, where the umbrella-like molecular structure of ammonia is inverted passing a planar transition state. The activation barriers of this reaction were simulated using the basis-set-free VQE approach and different classical methods with large basis sets, cf. Fig. 5. For larger basis sets, exact diagonalization is already unfeasible here. CISD, however, provides an accurate model for this reaction type since...
Figure 4. **Dissociation curve of the hydrogen molecule**: Energies are computed with a VQE (UpCCGSD) or classical methods (FCI). The Hamiltonians were constructed with basis-set-free methods (MRA) and Gaussian basis sets (GBS). All curves are denoted as method/basis($N_e$, $N_q$) with number of electrons $N_e$ and number of qubits $N_q$. Blue curves show GBS results with minimal (STO-3G) and slightly larger (6-31G) basis sets, while red curves show the UpCCGSD/MRA results with the same qubit requirements. Black curves show the best GBS results (the same in both panels). The two $H_2$/GBS-Opt curves show results for the individually optimized Gaussian basis sets (exponents, contraction coefficients, centers) according to Ref. 70. The MP2/MRA($N_e$, $N_q$) curves show the result of the classical surrogate model (PNO-MP2) for the Hydrogen molecule. The same orbitals are used for UpCCGSD/MRA($N_e$, $N_q$), illustrating the energy differences between the surrogate model and the VQE. FCI/CBS points were taken from Refs. 65, 71. Bond distances are given in Ångstrom.

Figure 5. **Umbrella reaction of ammonia**: Energy barriers in relation to qubit requirements. Results are computed with different classical methods and the basis-set-free VQE (UpCCGSD ansatz).

possible size-inconsistency issues are negligible in this intramolecular reaction, witnessed by the accompanied FCI calculations performed for the smaller basis-sets. Additional to the full treatment of the 10 electrons of ammonia, we used a 6 electron active space, freezing the lowest occupied Hartree–Fock orbital and the orbital corresponding to the lone pair of ammonia. Simulations with the small basis sets STO-3G and 6-31G over- or underestimate the activation barrier by more than a factor of two, while the basis-set-free approaches yields accurate energies. In this case, 12-18 qubits suffice for the basis-set-free approach to achieve a numerical accuracy, that would require 50-100 spin-orbitals with traditional basis sets.

### III. CONCLUSION & OUTLOOK

In this work, we developed a basis-set-free approach by using MRA-PNO-MP2 as a surrogate model to construct compact, system-adapted qubit Hamiltonians with high numerical precision. Initial demonstrations for absolute energies of atoms, small potential energy surfaces, and a toy model for a chemical reaction show a clear advantage of this approach compared to standard basis sets throughout all used metrics, allowing to achieve high numerical precision in the spatial representation of the wavefunction with significantly reduced number of qubits (see Tab. 1). Our approach is furthermore a promising candidate towards black-box quantum chemistry on quantum computers. In combination with adaptive circuit construction [73, 75], this approach opens a path towards fully adaptive quantum chemistry independent of static basis sets and ansatz models. Combinations of adaptive circuit construction with generalized pair approximations [56, 74] in the spirit of Ref. [61] are promising candidates towards accurate, adaptive, and computational feasible variational methods. Our ap-
The performance of the basis-set-free VQE. We developed methods are promising candidates to further improve the MP2 optimization. In the VQE context, approaches applied in the original formulation of the MRA-PNO-of explicitly correlated approaches, that were already and numerical accuracy can be expected in the context same way. Further improvements on qubit requirements be applied within the basis-set-free representation in the pressed representations \cite{63, 76}. These approaches could corrections \cite{37} or by using symmetries to obtain com-
proach is different in spirit as other approaches aiming to reduce the qubit requirements by applying external corrections \cite{37} or by using symmetries to obtain com-
pressed representations \cite{63, 76}. These approaches could be applied within the basis-set-free representation in the same way. Further improvements on qubit requirements and numerical accuracy can be expected in the context of explicitly correlated approaches, that were already applied in the original formulation of the MRA-PNO-MP2 optimization. \cite{36} In the VQE context, approaches using trans-correlated Hamiltonians have been demonstrated recently using LCAO representations. These methods are promising candidates to further improve the performance of the basis-set-free VQE. We developed the first applications that exploit the structure of the pair-natural orbitals. Independent on the underlying numerical representation, this leads to low-depth quantum circuits, allowing savings in the qubit and gate requirements. These approaches have the potential to play an important role in future developments, either as benchmarks for small quantum hardware, or as initial states for more sophisticated quantum algorithms as illustrated for BeH\textsubscript{2} in Fig. 6. In this work, we used MP2 as correlated surrogate model, but other models are also possible within this framework, and might bring additional advantages. A natural extension to MP2 is given by the coupled-cluster hierarchy, where models like CCD and CCSD first come to mind. More restricted models like pair-restricted coupled-cluster, that are also employed in quantum circuit construction \cite{56, 74},

Figure 6. Bond dissociation curves Total energies and errors with respect to the best affordable exact diagonalization (FCI) in the largest affordable Gaussian basis set (given in black). PNO-UpCC(S)D exploits the PNO structure of the surrogate model according to Eq. (9).
offer advantages through lower computational cost. In principle, more advanced surrogate models, that for example incorporate higher-order coupled-cluster terms only for the determination of specific orbitals, can be envisioned as well.

Notes Our implementations are open-source and available online through the TEQUILA package under github.com/aspuru-guzik-group/tequila, where we provide initial tutorials on the usage. A modified version of the MRA-PNO-MP2 implementation is available over a separate MADNESS branch under github.com/kottmanj/madness/tree/tequila. Feel free to contact JSK for more information and updates. The authors declare no competing financial interest.

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