

Effect of Orbital Localization Methods on Quantum Fragmentation and Embedding Accuracy

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Abstract - One of the critical challenges for near-term quantum technologies is implementing quantum embedding algorithms on current quantum hardware and developing new fragment stitching methodologies for quantum computers. In this paper, existing fragmentation and embedding methods and efficient implementations on a quantum computer are discussed. Particularly, orbital localization methods' effect on improving the accuracy of the fragmentation and embedding processes will be studied for the first time. Methods of fragmentation, embedding, localization and correlation were applied on smaller molecular systems as H_8 and H_4 . Both systems demonstrated an invariance in Bootstrap Embedding energy levels after various localization methods such as Löwdin, Boys, Pipek-Mezey, and IAO was applied. This invariance in energy levels validates the theoretical base of BE method, indicating that total molecular energy does not depend on localization of molecular orbitals. The high accuracy and fast results showed us the effectiveness of BE on larger molecular systems as it enhanced correlation and helped overcoming the possible obstacles. The aim is that these approaches will enable some of the first highly accurate calculations of large molecular systems and reactions on real quantum hardware.

Introduction

The accurate modeling of represents one of the most computationally challenging tasks in quantum chemistry, requiring a bridge between molecular motions and sufficiently accurate ab initio descriptions of electronic degrees of freedom. This can be highly computationally demanding on classical computers, and even beyond the reach of the largest supercomputers available. [1] Classical approaches are limited by the typically vast number of configurations needed to construct a chemically-accurate wave function. Even if one does not use Full Configuration Interaction (FCI), the exact method for solving the

Schrodinger Equation, methods like selected Configuration Interaction (sCI), [7,8,9] Configuration Interaction Singles, Doubles (CCSD), [10] or Coupled Cluster theory[11] still scale as the number of orbitals to a very high power.

Given the steep scaling of high-accuracy classical quantum chemistry methods, quantum computation has the potential of offering more exact quantum solutions at lower cost. In particular, quantum eigensolvers such as the Quantum Phase Estimation (QPE) algorithm[12] and Variational Quantum Eigensolver (VQE)[12] have demonstrated promising performance on quantum computers compared to classical methods, with the potential to produce highly accurate energies. [2] These energies can be used on their own to understand the energy levels of a molecular system, [13,14] or they can be combined with other methods, like machine learning potentials to produce force fields to run molecular dynamics calculations.[1,15]

Nonetheless,urrent quantum hardware suffers from restricted qubit counts, high error rates, and limited coherence times that collectively constrain the size and complexity of molecular systems that can be accurately modeled. [5,16,17] Hardware-efficient ansatze, which are quantum circuits that are specifically designed to overcome the limitations of quantum hardware. [62] may break Hamiltonian symmetries, while the need for repeated energy evaluations during VQE optimization introduces a computational overhead, caused by measurement noise and sampling errors. [5,63] These practical limitations of quantum hardware motivate the development of new quantum computing techniques for quantum chemistry that circumvent current error rates and qubit count restrictions, yet still accurately solve quantum chemistry problems.

Fragment embedding methods offer a solution to overcome the scaling limitations of both classical and quantum approaches by utilizing the locality of electron correlation. The fundamental principle of these methods is a divide-and-conquer strategy where computationally intensive, high-level theories are applied only to individual fragments rather than the entire system, reducing the size of the system that needs to be modeled and the consequent computational scaling. [18,21,44-46]

Over the years, many different classical fragmentation approaches have been introduced. [43,44] Standard fragmentation methods simply fragment a system and then reconstruct its total energy from those fragments. Recently, more sophisticated methods called embedding

theories have been developed. Classical embedding approaches such as Wave Function Embedding Theory and Density Matrix Embedding Theory (DMET) [4] treat embedded fragments as open quantum systems entangled to their surrounding bath, enabling treatment of strongly correlated systems. However, these methods often show slow convergence with fragment size due to surface errors at fragment-bath boundaries. Bootstrap embedding (BE), a new embedding method, (See Figure 1) addresses some of these limitations by employing overlapping fragments to reduce surface errors, though convergence challenges persist. [2]

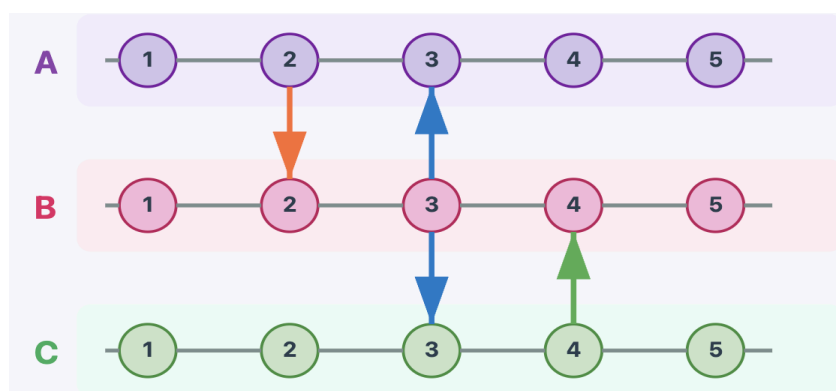


Figure 1: Figure explaining Bootstrap Embedding(BE) and potential overlaps

Thus far, bootstrap embedding has proven successful at reproducing the energies of large molecular systems, such as buckminsterfullerene, using just two- or three-atom fragments. [44-46] But, virtually all applications of bootstrap embedding to date have been performed on classical computers.

Quantum embedding extends these concepts by utilizing quantum hardware to solve individual fragments with high accuracy while using classical hardware to join the fragments. [21,42] This method is particularly useful because it generates fragments that are small enough for a quantum computer to compute while providing a path toward achieving solutions to much larger molecular problems.

This work addresses the critical challenge of implementing quantum embedding algorithms on near-term quantum hardware and developing novel fragment stitching methodologies for quantum computers. In the beginning, this paper by discussing the theory that underlies fragmentation and embedding methods and then proceed to discuss

how these can be efficiently implemented on a quantum computer. In particular, it will be demonstrated how using orbital localization methods can improve the accuracy of the fragmentation and embedding processes for the first time. [18-20] It is intended that these approaches will enable some of the first highly accurate calculations of large molecular systems and reactions on real quantum hardware.

Background Theory

Electronic structure is the field of quantum mechanics that aims to solve the time-independent Schrodinger Equation, whose solution provides important information about the likely locations and energies of particles in a quantum system. [22-23] Solving this problem is critical to developing new molecular therapeutics, designing new catalysts, and developing new quantum materials. [24-27,46]

The Schrodinger Equation may be posed as:

$$\hat{H} \Psi = E \Psi$$

Figure 2: The Schrödinger Equation

$\hat{H}$ is the total energy operator representing the sum of the kinetic and potential energies. The Hamiltonian acts on the wavefunction to generate energy eigenvalues. ψ describes the quantum state of a particle (the quantum wavefunction). $|\psi|^2$ gives the probability density of finding the particle at a given position. E represents the allowed energy levels of the quantum system. Each eigenvalue corresponds to a specific energy state.

Over the years, many classical methods have been developed to solve the electronic structure problem, including Density Functional Theory (DFT), [28,29] Hartree-Fock (HF) Theory, [30-32] and advanced wave function methods such as Coupled Cluster Theory [33] or Configuration Interaction theories. [34] While these techniques have become increasingly more accurate and efficient, they are still often accompanied by a very steep computational cost that scales, at worst exponentially, but at best, to a high-order polynomial, with system size. [35,36] This main reason why solving this equation is so expensive is because many possible many-body quantum configurations

may exist for a given system and finding the exact combination that describes a system correctly can be extremely subtle and time-consuming.

Quantum computers have the potential to overcome these scaling difficulties by more directly modeling quantum mechanics. One of the most popular algorithms for solving this Equation because of its practicality on modern, noisy-intermediate scale quantum computers is the Variational Quantum Eigensolver (VQE) algorithm, which is a member of the Variational Quantum Algorithm (VQA) family of algorithms. [12,37,38] The VQE algorithm is based on the Variational Principle in quantum mechanics, which states the optimal wave function of a system is the one that yields the lowest energy upon solving the Schrodinger Equation.

$$\min E(\theta) = \langle \psi(\theta) | \hat{H} | \psi(\theta) \rangle$$

Figure 3: Basis equation of VQE Algorithm

In the above equation, θ denotes the set of parameters that parameterize the wave function. $\min E(\theta)$ is used to denote the fact that the wave function with the optimal set of parameters will produce the lowest energy as a function of those parameters.

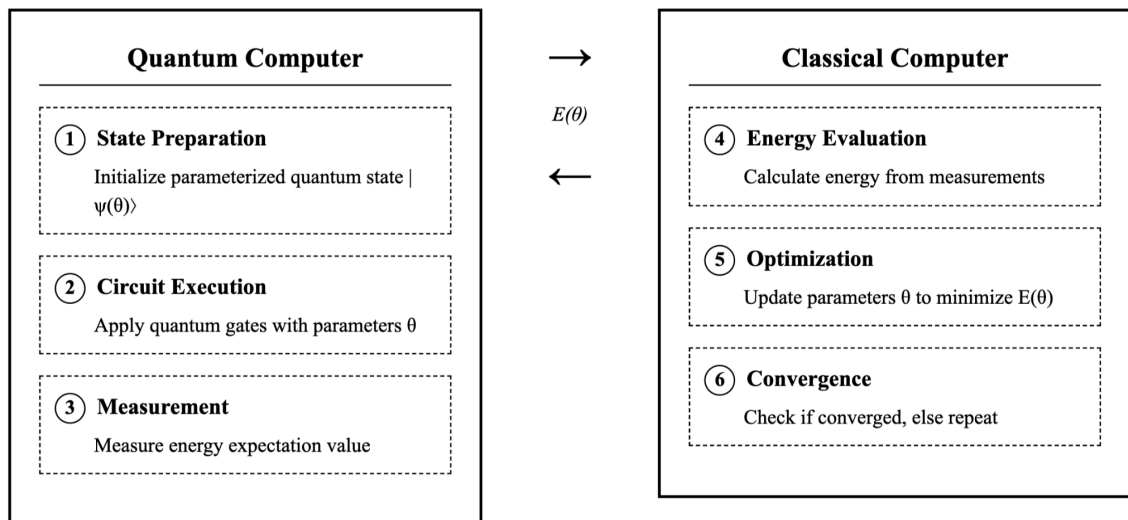


Table 1: Figure explaining the Variational Quantum Eigensolver (VQE) Algorithm

On a quantum computer, in VQE, one first constructs an initial wave function ansatz that is parameterized in different ways (see Figure 1). Then, one uses a quantum computer to find the energy of that parameterized wave function since a quantum computer is most efficient at solving the Schrodinger Equation. One subsequently uses that energy and its derivatives with respect to the parameters to modify the parameters of the wave function so as to further minimize the energy — and then iterates until the energy converges and the optimal wave function parameters are obtained.

The VQE algorithm begins by choosing a parameterized ansatz circuit $|\psi(\theta)\rangle$ and initializing the parameters θ (See Table 1). The quantum computer then prepares the quantum state and measures the Hamiltonian expectation value, which is sent to a classical computer to calculate the energy $E(\theta)$. A classical optimizer updates the parameters θ to minimize the energy, and this process repeats iteratively until convergence to the ground state is achieved. [37,38]

Quantum Computer Tasks	Classical Computer Tasks
Fragment Eigensolving: $H_{\text{emb}} \psi_i\rangle = E_i \psi_i\rangle$	Optimization: Update embedding potential V_{BE} based on matching conditions
SWAP Test Protocol: Measure overlap between fragment wavefunctions on boundary orbitals	Lagrangian Formulation: Solve constrained optimization with fragment matching constraints
Amplitude Amplification: Enhance measurement efficiency for density matrix elements	Convergence Check: Monitor self-consistency of fragment solutions

Table 2: Representation of Quantum Bootstrap Embedding Method with SWAP Test Protocol

There are many different potential forms for the VQE wave functions. Some forms are hardware-efficient and based on the hardware at one's disposal. [39] Others are based on chemical ansatzes like the wave function form from Unitary Coupled Cluster (UCC) theory. [37,40] These ansatzes come with different computational expenses depending upon their forms and the problem at hand. A straightforward VQE algorithm using UCC theory on a small molecule without truncations, for example, may require many thousands to millions of gates, which exceed the capacity of current quantum architectures. Thus, while VQE is a powerful algorithm, it still comes with its own costs, which limits what size molecular and material systems can be treated using VQE with chemical accuracy. [41,42]

Classical Fragmentation and Embedding Methods are useful techniques to reduce the difficulty of performing computationally demanding tasks, in our case, large molecular systems, by dividing the molecule in "fragments" to treat them individually and then combine in the end. [43] One of the best embedding techniques is Classical Bootstrap Embedding (BE), [44] in which overlapping fragments are used to create matching conditions to optimize the embedding. The key advantage that BE provides is the self-consistently improvable optimization that overlapping provides for faster convergence compared to other simple methods. [44,45] In other words, Bootstrap Embedding (QBE) iterates between quantum fragment solving and classical optimization until self-consistency is achieved in the embedding potential and fragment wavefunctions (see Table 2). QBE is particularly suited for quantum computers because it creates fragment sizes so small that they can fit onto the currently small quantum computers available. [46]

In a recent study on quantum embedding, it was shown that, instead of matching the qubit reduced density matrices (RDMs) element-by-element, the quantum matching algorithm can employ a SWAP test to match the full RDM between overlapping regions of the fragments in parallel for faster results. [46-48] Moreover, the quantum amplitude estimation algorithm [46,49,50] can enable even faster results to reach a certain accuracy on estimating the fragment overlap. In addition, the adaptive sampling changes the number of samples as the optimization proceeds in order to achieve increasingly accurate results.

Another crucial aspect that underlies many modern electronic structure methods such as embedding methods including Bootstrap Embedding (BE) is orbital localization theory. Localized molecular orbitals have helped us understand such classical chemical concepts as bonds, nonbonding electron pairs, core orbitals, and valency in terms of quantum

mechanics. [45,55] The main challenge is canonical molecular orbitals from Hartree Fock (HF) or Kohn-Sham (KS) theory are often delocalized across the entire molecular system. [51,53] Even though mathematical calculations of these orbitals are convenient, this delocalization makes chemical calculations and fragment-embedding difficult. [51,52] To solve this problem, localization techniques can be used to localize the orbitals around specific atoms, minimizing the orbitals' overlap with orbitals on other atoms. Localizing the orbitals involves rotating the initial, often canonical orbitals until they are most localized and have the smallest possible variation. [51, 54]

One of the earliest and most widely used localization schemes is the Boys localization method, developed by S. Francis Boys in 1960. [51] Boys' method minimizes the spatial extent of the occupied molecular orbitals, minimizing the function:

$$B = \sum_i^{N_P} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_1) \|\mathbf{r}_1 - \mathbf{r}_2\|^2 \phi_i^*(\mathbf{r}_2) \phi_i(\mathbf{r}_2),$$

Figure 4: Equation Representing Boys Localization Method

where ϕ_i are the localized orbitals and r_{12} represents the electron-electron repulsion operator. This can be re-expressed as:

$$B = 2 \sum_i^{N_P} \left(\int d\mathbf{r} \phi_i^*(\mathbf{r}) \|\mathbf{r}\|^2 \phi_i(\mathbf{r}) \right) - 2 \sum_i^{N_P} \left\| \left(\int d\mathbf{r} \phi_i^*(\mathbf{r}) \mathbf{r} \phi_i(\mathbf{r}) \right) \right\|^2.$$

Figure 5: Simplified equation of Boys Localization Method in Fig. 4

Since the traces of operators are invariant to unitary transformations, the task of finding the minimum of B is equivalent to maximizing the distances between orbital centroids or maximizing the sum of the squares of distances of orbital centroids from the origin of the coordinate system. [55,56] (See Figure 5) An alternative approach was also introduced by Gregory Wannier in 1937 in terms of localized orbitals, [57] which was followed by the Boys localization method. These methods are specifically crucial for modern electronic structure theory applications such as Quantum Bootstrap Embedding, [46] Density Matrix

Embedding (DMET) [58] that uses localized orbitals for the construction of the orbitals it uses, or Local Correlation Methods. [59] Modern developments include Intrinsic Atomic Orbitals (IAOs), which provide a better localization of orbitals. [60]

Moving toward working with larger molecular systems and more sophisticated quantum algorithms, the role of orbital localization will only become more central to achieving chemical accuracy that is also computationally achievable. [55-61] Localized orbitals make the computations more efficient by eliminating the need to consider large overlaps among orbitals across the system.

Computational Approach

The computational part is written in Python3 and can be divided into three parts, molecular system setting parameters, fragmentation parameters and localization parameters. To observe the effect of localization on a hydrogenic molecule, we first apply bootstrap embedding to a linear H_4 molecule, and then use localization methods on the post-bootstrapped molecule. Later, the BE and localization methods were repeated on a cubic H_8 molecule. The effect of localization on post-BE molecules is observed.

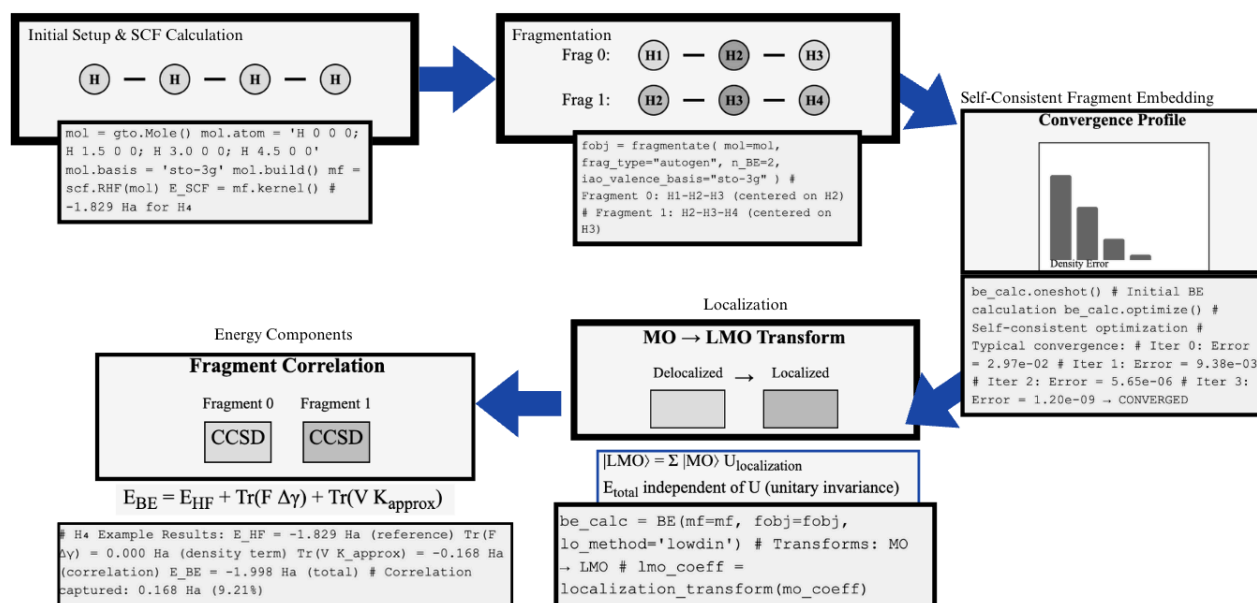


Figure 6: Schematic Workflow of Bootstrap Embedding Algorithm with Localization

The initial step is to set Standard SCF calculation for reference values (Standard Hartree-Fock reference), setting initial energy and molecular orbitals (See Figure 6). The next step is fragmentation, manual and auto-fragmentation methods were used, ensuring shared atoms are existing for further steps including correlation applications. As each fragment is in the bath of electronic field of other fragments, each fragment has an embedding potential of its environment so each fragment is affected by its neighbor fragments, to prevent the possible obstacles Bootstrap Embedding is applied to the fragmented molecules to benefit from its self-iterative features. The accuracy and computational usefulness for capturing electron correlation comes from this self-consistency of the BE. Then, various localization methods such as Löwdin, Boys, Pipek-Mezey, IAO the molecular orbitals are applied. Embedding the fragments first allows us more established fragment interactions and testing different localization methods on an embedded system. Finally, CCSD was applied to fragments to get more accurate results with correlation, as BE makes accurate correlation for systems where direct methods fail and could proceed to having wrong bond energies, molecular geometries or reaction energies.

```
# Reference Calculation
mf = scf.RHF(molecule)
E_SCF = mf.kernel() # Baseline energy

# Fragmentation Setup: Automatic or manual fragment definition
fragments = fragmentate(molecule, method="autogen", n_BE=2)

# Bootstrap Embedding - Main calculation with different localizations
for localization in ['lowdin', 'boys', 'pipek', 'iao']:
    be_calc = BE(mf, fragments, lo_method=localization)
    be_calc.oneshot() # Initial embedding
    be_calc.optimize() # Self-consistent refinement

    # Extract measurements
    energies[localization] = be_calc.ebe_tot
    orbitals[localization] = be_calc.lmo_coeff

# Comparative analysis
energy_differences = compare_localizations(energies)
correlation_scaling = analyze_system_size(H4_energy, H8_energy)
method_validation = check_invariance(energies)
```

Figure 7: Summary code of algorithm from reference calculation with Standard Hartree-Fock values, fragmentation, BE, localization and analysis of H₄ and H₈ systems.

BE was applied to both molecules and then localization method is used on the post-BE molecules to examine the effect of localization on BE method. (See figure 7) For fragmentation; autogen, chemgen and graphgen methods were examined (autogen is used in figure 7 as a representative), number of fragments (n_BE), overlap information and bath orbital information were used. Localization methods such as lodwin, boys, pipek, iao from the QuEmb documentation were used and showed in the code to comparing localization effects.

```

One Shot BE
Solver : CCSD

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BE ENERGIES with cumulant-based expression
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E_BE = E_HF + Tr(F del g) + Tr(V K_approx)
E_HF      : -1.82913741 Ha
Tr(F del g) : 0.00000001 Ha
Tr(V K_approx) : -0.16848670 Ha
E_BE      : -1.99762411 Ha
Ecorr BE   : -0.16848670 Ha

```

Fig 8 : Figure of the code written in python from QuEmb package demonstrating BE method applied on a H₄ system. The Bootstrap Embedding Energy Formula ($E_{BE} = E_{HF} + \text{Tr}(F \text{ del } g) + \text{Tr}(V K_{\text{approx}})$) is given and the measured energies are shown separately.

As for a solver method, or correlation, CCSD method was used from the same documentation. (See Figure 8) Energy after BE was measured, specifically, Hartree-Fock reference energy(E_{HF}), total bootstrap embedding energy(E_{BE}), the correlation contribution ($\text{Tr}(V K_{\text{approx}})$), the total correlation energy ($E_{\text{corr BE}}$) and fragment energies were measured. $\text{Tr}(F \text{ del } g)$ accounts for density changes.

Additionally, properties of localized molecular orbitals were measured. Optimization was made with convergence (CCSD) and fragment behaviors were analysed. PySCF was used for reference calculations, results obtained are -1.829 Hartree for H₄ and -3.217 Hartree for H₈. Then, by using QuEmb documentation autogenerated 2 fragment approach was used.



Figure 9: Linear H_4 chain with 2 fragment approach. Algorithm includes overlapping 3 atom fragments. (H_1, H_3 centered on H_2 and H_2, H_4 centered on H_3)

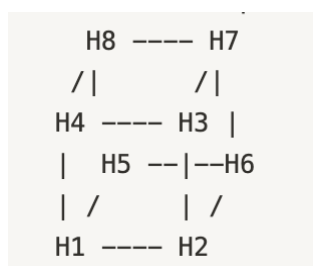


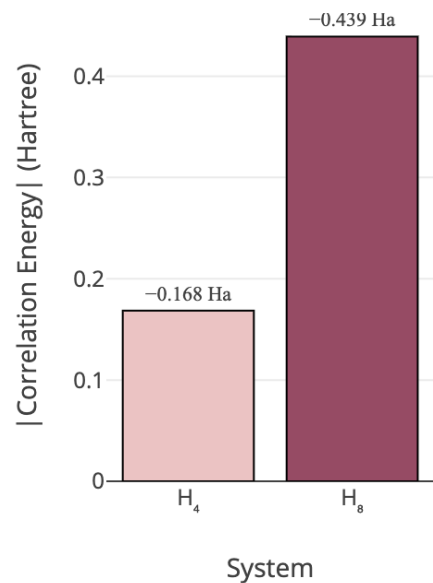
Figure 10: molecular graph representation of H_8 molecule.

For H_4 since it is a simple linear chain manual fragmentation was used (See Figure 9), however H_8 required more complex calculations for fragmentations due to its cubic system therefore an automatic algorithm was preferred. (See Figure 10)

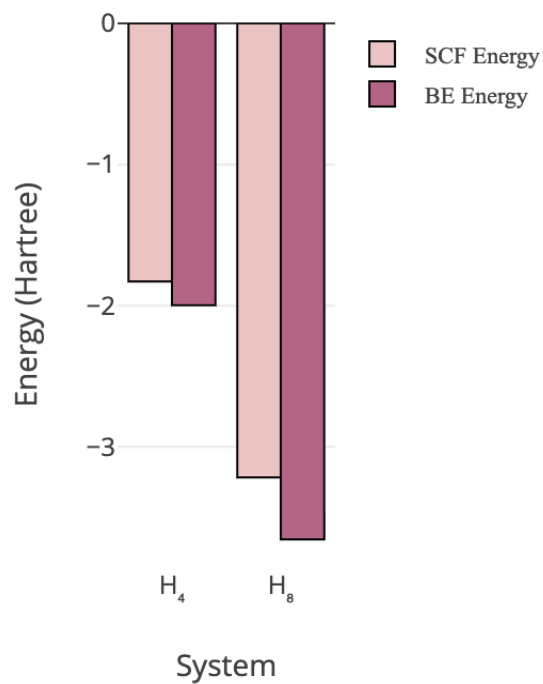
Results

All calculations performed with STO-3G basis set and QuEmb documentation using 2-fragmented systems. The invariance of BE energies under different localization methods validates the accuracy of the bootstrap embedding approach for hydrogen cluster systems.

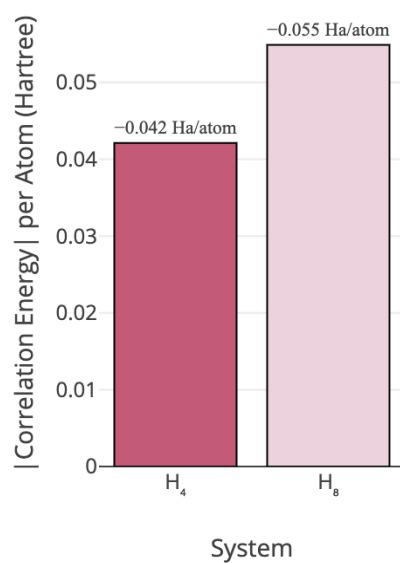
H_4 Self-Consistent Field (SCF) energy is -1.82913741 Hartree, BE energy is -1.99762411 Hartree, correlation energy is -0.16848670 Hartree, correlation per atom energy is -0.04212168 Hartree/atom. Bootstrap Embedding performance for 2+2 fragmented H_4 system showed an increase in energy after BE ($E_{BE} - E_{SCF}$) of 0.168487 Hartree and a moderate correlation as 9.21% of total energy. H_8 SCF energy is -3.21749723 Hartree, BE energy is -3.65664793 Hartree, correlation energy is -0.43915070 Hartree, correlation per atom energy is -0.05489384 Hartree/atom



Graph 1: Energy comparison between SCF and BE total energies for both H_4 and H_8 systems, demonstrating significant correlation energy capture.

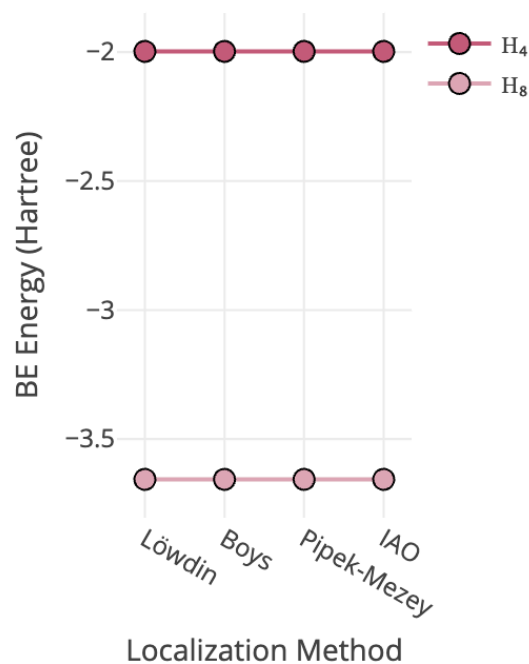


Graph 2: Correlation energy scaling from H_4 to H_8 ($2.61\times$) due to increased electron correlation effects in larger hydrogen clusters.



Graph 3: Per-atom correlation energy comparison, demonstrating high transferability with near values (-0.042 vs -0.055 Ha/atom), indicating consistent correlation treatment across system sizes.

Correlation scaling of H_8/H_4 is 2.6064 thus we can conclude that H_8 has 2.61x more correlation than H_4 and we measure that per-atom scaling is 1.3032 Hartree



Graph 4: Localization method invariance analysis, confirming identical BE energies across Löwdin, Boys, Pipek-Mezey, and IAO localization schemes.

For H_4 all Löwdin, Boys, Pipek-Mezey and IAO localization methods applied to the post-BE molecule showed an invariance in energy. All measured identically -1.99762411 Hartree. For H_8 as well, all BE energy was equal to -3.65664793 Hartree after each localization method. Thus, we can conclude that BE energy is invariant under localization for both H_4 and H_8 systems.

To conclude, from our experiments we can observe an invariance of BE energies across all localization methods. Reasonably, H_8 has more correlation compared to H_4 and correlation for each atom was consistent between the two systems by 1.30x ratio of H_8/H_4 . Both systems converged quickly due to working on simpler systems, H_4 showed immediate convergence and H_8 converged in nearly 3 iterations indicating that BE is working correctly for both systems, reducing the computational-cost and error reduction.

Discussion

The main goal of this study is to observe the effects of localization methods on post-BE systems to be able to better understand the role of localization in fragmentation and embedding techniques. After running fragmentation, embedding, localization and correlation methods on smaller systems as H_8 and H_4 , we observed an invariance in Bootstrap Embedding energy levels after applying localization. Across both H_4 and H_8 systems, total bootstrap embedding energies remained identical to at least eight decimal places when using Löwdin, Boys, Pipek-Mezey, and IAO methods. However, the high accuracy and fast results showed us the effectiveness of BE on larger molecular systems as it enhanced correlation and helped overcoming the possible obstacles. Plus, this invariance we obtained validates the theoretical base of BE method, indicating that total molecular energy does not depend on localization of molecular orbitals.

The invariance also shows the effectiveness of self-continuous embedding techniques, since self-consistency is achieved before localization energy levels are the same. Even applying localization after embedding fragments didn't show any effect on energy levels, it showed us that the BE method worked successfully as we observed a rapid convergence of nearly 3 iterations. Timing of the localization can be changed in order to examine change in energy levels and for more effective embedding approaches.

Conclusions

We applied bootstrap embedding on a linear H_4 molecule, followingly use localization such as Löwdin, Boys, Pipek-Mezey, and IAO methods on the post-bootstrapped molecule. Later, we reapply the BE and the same localization methods on a cubic H_8 molecule to observe the effect of localization on a hydrogenic molecule. The localization methods that were applied to post-BE systems showed an invariance in energy levels of post-BE systems, we can conclude from our experiments with the QuEmb documentation, the localization methods (Löwdin, Boys, Pipek-Mezey, and IAO) applied on post-BE molecular systems, the Bootstrap Energies show an invariance towards localization in both H_8 and H_4 systems.

While total energy levels after the localization is applied remained unchanged, different localization methods (Löwdin, Boys, Pipek-Mezey, and IAO) demonstrated different orbital coefficient structures. This means that most preferable localization method can be choosed without any change in energy. Localization method is also a crucial part of BE method. However, the invariance of energies after the localization method enables us to better understand the role and benefits of BE, we can observe more clearly its high capacity.

For future studies, localization methods can be selected regrading the computational convenience, alignment with research purposes, chemical insight without any concern regarding correlation energies and experiments can be repeated in larger molecular systems if there is no computational limitations. This paper is a representative study to observe the effects of localization on post-BE molecular systems, and therefore stands as a modal for studies with larger molecular systems, since it would be computationally challenging and expensive to observe the effects of the mentioned localization methods on post-BE structures for larger molecular systems.

Acknowledgements

This work is supported by Python3 and QuEmb repository containing BE methods and quemb.molbe and quemb.kbe libraries. The code provided in the QuEmb documentation uses PySCF library for quantum chemistry calculations enabling parallel computations in hgih-performance computing environments. (QuEmb Documentation)

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