Intractability of Electronic Structure in a Fixed Basis

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(Received 5 October 2021; revised 18 January 2022; accepted 14 March 2022; published 2 May 2022)

Finding the ground-state energy of electrons subject to an external electric field is a fundamental problem in computational chemistry. While the theory of QMA-completeness has been instrumental in understanding the complexity of finding ground states in many-body quantum systems, prior to this work it has been unknown whether or not the special form of the Hamiltonian for the electronic structure of molecules can be exploited to find ground states efficiently or whether the problem remains hard for this special case. We prove that the electronic-structure problem, when restricted to a fixed single-particle basis and a fixed number of electrons, is QMA-complete. In our proof, the local Hamiltonian is encoded in the choice of spatial orbitals used to discretize the electronic-structure Hamiltonian. In contrast, Schuch and Verstraete have proved hardness for the electronic-structure problem with an additional site-specific external *magnetic* field, but without the restriction to a fixed basis, by encoding a local Hamiltonian on qubits in the site-specific magnetic field. We also show that estimation of the energy of the lowest-energy Slater-determinant state (i.e., the Hartree-Fock state) is nondeterministic polynomial time (NP)-complete for the electronic-structure Hamiltonian in a fixed basis.

DOI: 10.1103/PRXQuantum.3.020322

I. INTRODUCTION

The simulation of quantum-mechanical systems is one of the most important computational challenges in modern science. The solution of this problem, broadly defined, will allow us to probe the foundations of physics, chemistry, and materials science, and will have useful applications to a wide variety of industries. On the other hand, the very properties that make quantum-mechanical systems so interesting—such as the exponential growth of the underlying state space and quantum entanglement—also make quantum simulation a particularly difficult computational task.

Finding the means to tame this daunting complexity is an objective that is nearly as old as quantum mechanics itself. Paul Dirac, in a foundational paper from 1929, asserted that "The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation" [1].

Today, nearly a century later, Dirac's quote captures the underlying motivation for a large body of quantum science research. For example, in the context of simulating systems of many electrons, the complexity inherent in the simulation problem has been addressed by approximation methods such as Hartree-Fock and density-functional theory [2], as well as by considering simplified quantum models such as the Hubbard and Heisenberg Hamiltonians [3]. Moreover, even in a new, exciting era in which noisy, intermediate-scale quantum computers are being developed that may be well suited to solve certain quantum simulation problems, Dirac's wisdom prevails. Existing quantum algorithms, such as the phase-estimation algorithm and the variational quantum eigensolver, all obtain approximate solutions to special cases of the quantum simulation problem (see, e.g., Refs. [4–6]).

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However, there are also fundamental limitations to these simulation algorithms that stem from quantum computational complexity. Kitaev, building on the classical work of Cook and Levin, has proved that a very general quantum simulation problem—approximating the ground-state energy of a k-local Hamiltonian—is QMA-complete [7, 8]. QMA is a natural quantum analog of nondeterministic polynomial time (NP), and QMA-complete problems should not have an efficient quantum algorithm, for essentially the same reasons that NP-complete problems (such as Boolean satisfiability) should not have efficient classical algorithms.

Nonetheless, QMA-completeness should not be interpreted as a categorical roadblock but, rather, as an important guidepost for the development of future quantum algorithms. In the same way that many practically interesting instances of classical constraint satisfaction problems have special structural properties that avoid the worst-case hardness implied by NP-completeness results, we study QMA-completeness in order to understand which structural properties reduce the complexity of the simulation problem—and which properties do not—enabling improved quantum simulation algorithms that could potentially exploit this structure.

In the case of qudit Hamiltonians, many subsequent results have helped discover the landscape of these structural properties. For instance, we know that QMA-completeness persists even if the terms are 2-local on a two-dimensional (2D) lattice of qubits [9], are all the same up to a positive rescaling [10], or are translationally invariant in one dimension (but for high local dimensions) [11]. On the other hand, much less is known about local Hamiltonians acting on indistinguishable particles. The current state of knowledge is summarized in Table I. Note that, despite a wealth of numerical work, hardly anything is rigorously known about the boundary between easy and hard electronic structure instances, and there is no well-defined nontrivial family of instances that is known to be in bounded-error quantum polynomial time (BQP). Crucially, we do not know if the special form of the Hamiltonian for the electronic structure of molecules can be exploited by efficient algorithms to decide the ground-state energy or if this restricted problem remains intractable. This problem is of particular interest since simulating quantum chemistry is often heralded as an important application for near-term quantum computers.

Our results take an important step toward answering this question. We show that when restricted to a fixed number of electrons and a fixed single-particle basis, approximation of the ground-state energy of the electronic-structure Hamiltonian is QMA-complete. This can be interpreted as a direct sharpening of Dirac's quote: we conclusively demonstrate that these properties *do not* add enough structure to enable the existence of an efficient quantum simulation algorithm to approximate the ground-state energy of such systems. We conclude with the formalization of two variants of the electronic-structure problem that get even closer to capturing the true goal of quantum chemistry. These formal problem statements constitute part of the contribution of this work; to apply the tools of complexity theory to real-world problems, as we do here, the essence of practitioners' goals must be formalized precisely before the achievability of those goals can be definitively determined. We hope that, by doing so here, we lay the foundation for future work on the computational complexity of quantum chemistry.

II. THE ELECTRONIC-STRUCTURE PROBLEM

The local Hamiltonian problem for systems of indistinguishable particles has two distinctive features. First, the Hamiltonians themselves are invariant under permutations of the particles. Second, the goal is to estimate the lowest energy of a symmetric (for bosons) or antisymmetric (for fermions) state. In this work, we consider the local Hamiltonian problem for fermionic systems. Generic Hamiltonians (i.e., quartic polynomials in the elementary operators with general coefficients) for both types of indistinguishable particles have been shown to be QMA-complete [13,15], but, as with Hamiltonians on distinguishable particles, we can ask: how hard are more physically realistic classes of Hamiltonians? Physically

TABLE I. Known results for physically realistic Hamiltonians. The result for qubits is representative but many similar results are known (see, e.g., Refs. [11,12]). The results for bosons and fermions are exhaustive, to the knowledge of the authors.

Particle	Hamiltonian	State	Complexity	Instance encoding	Reference
Qubits	2D semitranslationally invariant	Quantum	QMA-complete	Coefficients	[10]
Bosons	Two-body	Quantum	QMA-complete	Coefficients	[13]
Bosons	Bose-Hubbard	Quantum	QMA-complete	Graph	[14]
Fermions	Two-body	Quantum	QMA-complete	Coefficients	[15]
Fermions	Two-body	Slater determinant	NP-complete	Coefficients	[16]
Fermions	Electronic structure (with magnetic field)	Quantum	QMA-complete	Magnetic field	[16]
Fermions	Electronic structure (fixed basis)	Quantum	QMA-complete	Basis	This paper
		Slater determinant	NP-complete		This paper
Fermions	One-body		P		

realistic Hamiltonians on indistinguishable particles have special properties that could make them more amenable to computing ground energies. In particular, here we are focused on the computational complexity of the *electronic structure (ES) Hamiltonian*

$$H^{(\mathrm{ES})} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i V(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (1)$$

which acts on an antisymmetric state $\psi : \mathbb{R}^{\eta\times 3} \to \mathbb{C}$ of η electrons, where $\mathbf{r}_i$ is the position of the ith electron in three-dimensional (3D) space. For η electrons and a specified electric potential $V : \mathbb{R}^3 \to \mathbb{R}$, this is the Hamiltonian dictated by the laws of electromagnetism. Of particular interest in chemistry is the *molecular electronic-structure Hamiltonian*, in which the external potential

$$V(\mathbf{r}) = -\sum_j \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|} \quad (2)$$

is that of nuclei modeled as classical point particles, each with positive charge Z_j and located at fixed position $\mathbf{R}_j$. In reality, the nuclei are also quantum particles but they are so much more massive than the electrons that this model (the *Born-Oppenheimer* approximation) is usually a sufficiently accurate approximation to the Hamiltonian of a molecule specified by the nuclear charges and number of electrons. There is a separate optimization procedure to find the lowest-energy configuration of nuclear positions.

Physically, the wave function of the electrons is over continuous real space. Computationally, we need to discretize the space of possible wave functions in some way in order to have a finite representation of a potential ground state. This leads to the fundamental computational problem of quantum chemistry, estimation of the ground-state energy of the *electronic-structure Hamiltonian in a fixed basis*:

$$H^{(\mathrm{ES})}(\boldsymbol{\phi}, V) = T + V + U \quad (3)$$

$$= \sum_{\substack{i,j\in[n]\\ \sigma\in\{\pm1\}}} (t_{i,j} + v_{i,j}) a^\dagger_{i,\sigma} a_{j,\sigma} \quad (4)$$

$$+ \frac{1}{2}\sum_{\substack{i,j,k,l\in[n]\\ \sigma,\tau\in\{\pm1\}}} u_{i,j,k,l} a^\dagger_{i,\tau} a^\dagger_{j,\sigma} a_{k,\sigma} a_{l,\tau}, \quad (5)$$

where $\boldsymbol{\phi} = (\phi_1, \ldots, \phi_n)$ is the single-particle basis with elements $\phi_i : \mathbb{R}^3 \to \mathbb{C}$ and

$$t_{i,j} = -\frac{1}{2}\int d\mathbf{r}\, \phi_i^*(\mathbf{r}) \nabla^2 \phi_j(\mathbf{r}), \quad (6)$$

$$v_{i,j} = \int d\mathbf{r}\, \phi_i^*(\mathbf{r}) V(\mathbf{r}) \phi_j(\mathbf{r}), \quad (7)$$

$$u_{i,j,k,l} = \int d\mathbf{r} d\mathbf{s}\, \phi_i^*(\mathbf{r}) \phi_j^*(\mathbf{s}) \frac{1}{|\mathbf{r} - \mathbf{s}|} \phi_k(\mathbf{s}) \phi_l(\mathbf{r}). \quad (8)$$

The indices $i, j, k, l \in [n]$ index spatial orbitals and $\sigma, \tau \in \{\pm 1\}$ indicate the spin. For each spatial orbital $\phi_i(\mathbf{r})$, there are two spin orbitals $\phi_{i,\pm1}(\mathbf{r})$. We use ± 1 as an index for simplicity but, of course, physically the spin of the electron has magnitude $1/2$ (in atomic units). Given the potential $V(\mathbf{r})$ and a fixed set of orbitals, the Hamiltonian shown in Eq. (3) is then completely determined by the integrals for the kinetic and potential energy shown in Eqs. (6)–(8). This leads to the following computational problem.

A. Electronic structure in a fixed basis

An instance of electronic structure in a fixed basis is specified by an external electric field $V : \mathbb{R}^3 \to \mathbb{R}$, a number η of electrons, a basis $\boldsymbol{\phi} = (\phi_1, \ldots, \phi_n)$, and thresholds $a < b$, where $b - a \geq 1/\mathsf{poly}(\eta)$. The external potential V and the basis $\boldsymbol{\phi}$ must be specified concisely [using $\mathsf{poly}(n)$ bits] in a way that allows for efficient [$\mathsf{poly}(n)$-time] calculation of the integrals in Eqs. (6)–(8). The goal is to determine whether the ground-state energy of H_{ES} in the subspace of η electrons spanned by the given basis is at most a or at least b.

This is the version of the problem posed by Whitfield *et al.* [17], who left its hardness as an open problem. We answer here in the affirmative by showing a family of single-particle bases that encodes hard problems; our result shows hardness both when there is no external potential [$V(\mathbf{r}) = 0$] and when the external potential is due to positive point charges at fixed positions (i.e., classical nuclei in the Born-Oppenheimer approximation).

Our definition of the problem allows for states with arbitrary total spin, and this freedom is critical in our construction. One can also consider a variant in which the total spin is fixed, analogous to, for example, the XY problem with fixed magnetization. Our definition of the problem also restricts the states allowed to a finite-dimensional space spanned by a set of fixed single-electron orbitals. By necessity, this is the form of the problem solved in practice by computational chemists. However, for practical purposes, it is desirable that the ground state or ground energy in the chosen basis be close to that in a complete infinite-dimensional basis. The difference between these two is known as the basis-set error, and bases are typically chosen in order to minimize this error. The basis we use in our construction is artificial in this sense; in the absence of an external potential, there is nothing to confine the electrons to the subspace of $\mathbb{R}^3$ spanned by this particular basis. However, the orbitals that we use are still superpositions of Gaussians, a commonly used form in computational chemistry; for example, the basis functions in the STO-3G basis set [18] are composed of a fixed superposition of three primitive Gaussians. Indeed, we prove the following theorem that the electronic-structure problem in a fixed

basis is QMA hard by encoding a QMA-hard Hamiltonian in the construction of the basis. We use linear combinations of Gaussians because of the nice analytic form of the relevant integrals. Gaussians cannot precisely model the cusps at the nuclei [19], though we expect that this is inessential to our results. That is, we expect that Theorem 1 would hold for, e.g., linear combinations of Slater-type orbitals.

Theorem 1: (electronic structure in a fixed basis is QMA-complete, informal). *The electronic-structure problem in a fixed basis and at fixed particle number is QMA-complete, both with no external potential and with a nuclear potential.*

We prove Theorem 1 without an external potential in Appendix C and in Appendix D we prove the version with a nuclear potential as Corollary 1.

Other variants of the electronic-structure problem have been considered. Schuch and Verstraete show QMA hardness for electronic structure with an additional site-specific magnetic field (without restricting to a fixed basis), which is used to encode an instance of a QMA-hard problem [16]. Their result is thus incomparable to ours; we remove the magnetic field, but their problem does not require a fixed basis. The problem we prove to be hard is much closer to that solved in practical quantum chemistry: typically, molecular problems do not have external magnetic fields, let alone ones that can take on arbitrary values at different points in space.

III. HARDNESS OF ELECTRONIC STRUCTURE

The proof that electronic structure in a fixed basis is QMA hard proceeds in two stages. We first reduce from the antiferromagnetic Heisenberg Hamiltonian to the Fermi-Hubbard Hamiltonian in Sec. III A. Then we reduce from Fermi-Hubbard to electronic structure in a fixed basis in Sec. III B.

A. First step: Hardness of the Fermi-Hubbard Hamiltonian

This section gives an overview of the first reduction.

The Bose-Hubbard and Fermi-Hubbard Hamiltonians are as follows:

$$H^{(\mathrm{BH})} = \sum_{i\in V} U n_i(n_i-1) + \sum_{\{i,j\}\in E} t_{i,j}\left(b_i^\dagger b_j + \mathrm{h.c.}\right), \quad (9)$$

$$H^{(\mathrm{FH})} = \sum_{i\in V} U n_{i,+}n_{i,-} + \sum_{\{i,j\}\in E,\sigma\in\{\pm\}} t_{i,j}\, a_{i,\sigma}^\dagger a_{j,\sigma}, \quad (10)$$

where $G=(V,E)$ is the interaction graph and $a_i a_j^\dagger + a_j^\dagger a_i = b_i b_j^\dagger - b_j^\dagger b_i = \delta_{ij}$. When we refer to the "Hubbard" model without qualification, we mean the *Fermi*-Hubbard model, in which the particles are fermions. Hubbard Hamiltonians are of practical interest because they approximate Hamiltonians of many more complicated condensed-matter and chemical systems. Their solutions are taken to qualitatively describe those of the approximated systems.

Childs *et al.* [14,20] show that the Bose-Hubbard Hamiltonian and XY Hamiltonian are QMA hard with uniform coefficients. In both cases, because the coefficients are uniform, the instance is encoded entirely in the graph, which does not seem embeddable in, say, three spatial dimensions, as we would want for a physically realistic Hubbard Hamiltonian. Schuch and Verstraete [16] show as an intermediate result that the Fermi-Hubbard Hamiltonian on a 2D lattice with a site-specific *magnetic field* is QMA hard; the instance is encoded entirely in this magnetic field. We show that the magnetic field is not necessary, at the cost of having an arbitrary weighted interaction graph.

Theorem 2: (FH is QMA-complete). *The Fermi-Hubbard Hamiltonian with arbitrary coefficients and fixed particle number is QMA-complete, even if all of the tunneling coefficients have the same sign and are bounded by a polynomial in the number of particles.*

We prove Theorem 2 rigorously in Appendix B and present a sketch here. The proof reduces from the antiferromagnetic Heisenberg Hamiltonian:

$$H^{(\mathrm{Heis})} = \sum_{\{i,j\}\in E} \kappa_{i,j} W_{i,j}, \quad W = (II + XX + YY + ZZ)/2, \quad (11)$$

which is known to be QMA hard [10,21]. As in related previous constructions, we fix the number of particles to equal the number of spatial orbitals, i.e., half the number of spin orbitals. The large on-site-repulsion term U penalizes two electrons occupying the same spatial orbital and so the ground space of the repulsion term has exactly one electron in each spatial orbital. As has been done in Ref. [15], the spin of the electron in each orbital encodes a logical qubit. With the repulsion term dominating the Hamiltonian, we treat the rest perturbatively. To second order, this yields an antiferromagnetic Heisenberg Hamiltonian on the same graph as a Hubbard Hamiltonian. We go between a qubit Hamiltonian and a fermionic Hamiltonian using the Jordan-Wigner transformation $a_i \leftrightarrow \prod_{j<i} Z_j (X_i + iY_i)/2$. In general, this transforms local fermionic Hamiltonians into nonlocal qubit Hamiltonians, but with a particular ordering of the spin orbitals, the parity strings $\prod_{j<i} Z_j$ cancel out. In our case, this yields the local Heisenberg Hamiltonian.

B. From Fermi-Hubbard to electronic structure

We reduce from Fermi-Hubbard to electronic structure in a fixed basis by starting with an instance of

Fermi-Hubbard and creating a set of orbitals such that the resulting Hamiltonian given by Eq. (3) closely approximates the input Fermi-Hubbard Hamiltonian. The interaction graph for the input Hamiltonian has an edge for every pair of fermions with a nonzero interaction term. Given a Hamiltonian of this form, we create a set of orbitals corresponding to the vertices in the interaction graph. ϕ_i is the orbital for vertex i. Each ϕ_i is a superposition of what we call *primitive* orbitals, which are just Gaussians centered at various points in space. For the most part, these points are spaced out from all the other points by a parameter Γ, which is set to be large. For every edge $\{i,j\}$ in the interaction graph of the Fermi-Hubbard Hamiltonian, there is a pair of primitive orbitals, one in ϕ_i and one in ϕ_j, such that the two primitive orbitals are a distance $\gamma_{i,j}$ apart. The values of the $\gamma_{i,j}$ are small compared to Γ.

The dominant term that emerges from this construction is the kinetic energy between two Gaussians with exponent α that are separated by a distance of $\gamma_{i,j}$ (with a slight correction due to the fact that the Gaussians are not exactly pairwise orthogonal). Each distance $\gamma_{i,j}$ can then be tuned to obtain the desired coefficient to encode the Fermi-Hubbard Hamiltonian. Each orbital also includes a primitive orbital with exponent $\beta > \alpha$ in order to increase the on-site-repulsion term, ensuring that the ground space for the effective Hamiltonian has exactly one electron per spatial orbital. Thus, each of our orbitals has the form

$$\phi_i(\mathbf{r}) = 2^{-1/2}\phi_{i,0}(\mathbf{r}) + (2d)^{-1/2}\sum_{i=1}^{d}\phi_{i,l}(\mathbf{r}), \tag{12}$$

where each $\phi_{i,l}$ is a Gaussian and the parameter d is an upper bound on the degree of the graph. The functions $\phi_{i,0}$ all have some large exponent β and are therefore more concentrated than the functions $\phi_{i,l}$ for $l > 0$ which have a smaller exponent α. The construction is illustrated in Fig. 1 with a small example.

We use three approximation steps that ultimately show that the electronic-structure Hamiltonian $H^{(\mathrm{ES})}$ closely approximates the Fermi-Hubbard Hamiltonian $H^{(\mathrm{Hubb})}$:

$$H^{(\mathrm{ES})} \overset{\text{Sec. } C2}{\to} H^{(\mathrm{round})} \overset{\text{Sec. } C3}{\to} H^{(\mathrm{main})} \overset{\text{Sec. } C4}{\propto} H^{(\mathrm{Hubb})}. \tag{13}$$

Each step introduces some small error, the bounding of which constitutes the bulk of the technical work in our proof.

The transition from $H^{(\mathrm{ES})}$ to $H^{(\mathrm{round})}$ includes two approximation steps. The first approximation arises from the fact that the orbitals $\boldsymbol{\phi}$ that we use are not perfectly orthonormal. However, there is an orthonormal basis $\tilde{\boldsymbol{\phi}}$ that is very close to $\boldsymbol{\phi}$. We show that the difference is sufficiently small that we can proceed with the coefficients from the nonorthonormal basis but using the elementary operators of the orthonormal basis. There is one exception to this approximation: the overlap of the Gaussians that are relatively close (distance $\gamma_{i,j}$ apart) has a non-negligible effect and requires a slight correction to the corresponding kinetic energy coefficient. In the second approximation step, we drop the interactions of primitive orbitals that are at least a distance of Γ apart, resulting in an expression with many fewer terms. The effect of applying both approximations results in the Hamiltonian $H^{(\mathrm{round})}$. The transition from

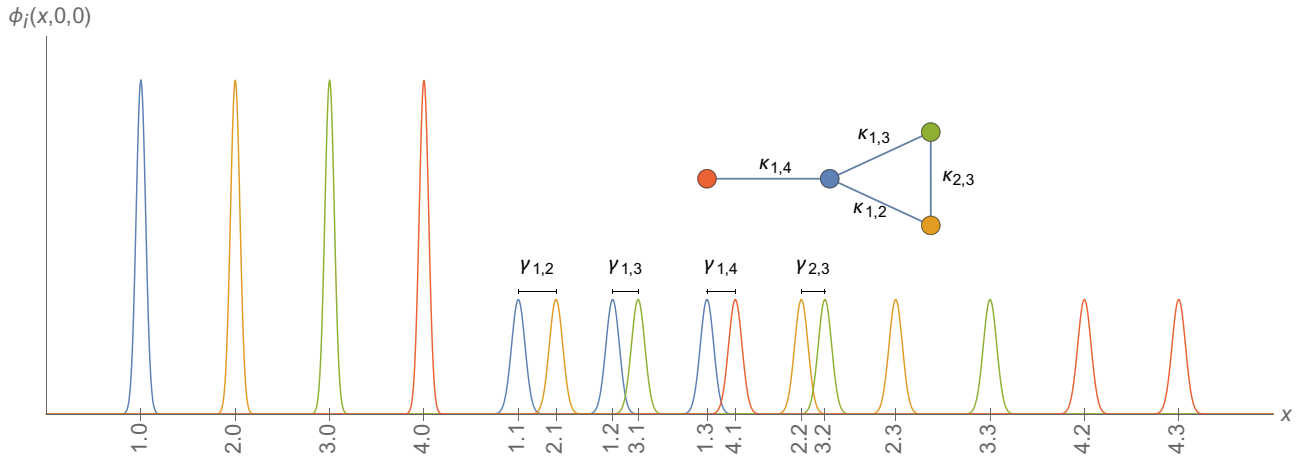

FIG. 1. The inset shows the interaction graph of a Heisenberg Hamiltonian with coefficients $\{\kappa_{i,j}\}_{\{i,j\}\in E}$ as in Eq. (11). It has degree $d = 3$. Each vertex is associated with a composite orbital $\phi_i(\mathbf{r})$ as in Eq. (12). $\phi_i(\mathbf{r})$ is a sum of primitive Gaussian orbitals centered at points $\mathbf{x}_{i,0}, \ldots, \mathbf{x}_{i,d}$, where the Gaussian centered at $\mathbf{x}_{i,0}$ has more weight and a larger exponent. The orbitals are color coded according to which vertex they belong to from the interaction graph and thus to which composite orbital they contribute. For example, the orbital associated with the blue vertex in the interaction graph would be a superposition of the blue Gaussians. In this example, all of the points $\mathbf{x}_{i,l}$ are arranged along a single line, but the only requirements are that (1) for every edge $\{i,j\}$ in the Heisenberg graph, the corresponding pair of points is separated by $\gamma_{i,j}$ and (2) otherwise all centers are $\Gamma \gg \gamma_{\max}$ away from each other.

$H^{(\mathrm{round})}$ to $H^{(\mathrm{main})}$ involves dropping the potential-energy terms that involve more than one primitive orbital. The difference between $H^{(\mathrm{round})}$ and $H^{(\mathrm{main})}$ is an energy offset that is constant for a fixed number of electrons plus an error term that we bound in the proof. We then show that the parameters can be set so that the coefficients of $H^{(\mathrm{main})}$ approximate the Fermi-Hubbard model to within any inverse polynomial.

IV. HARDNESS OF LOWEST-ENERGY SLATER DETERMINANT

The methods we develop for proving the hardness of electronic structure can also be used to show the hardness of a commonly used variant of electronic structure known as Hartree-Fock. Classical algorithms for finding the ground-state energy of quantum Hamiltonians are often limited by the fact that the ground state seems to have no concise classical description. For that reason, chemists often try to find the lowest-energy Slater determinant, known as the Hartree-Fock state. Within a fixed basis $\boldsymbol{\phi} = (\phi_1, \ldots, \phi_n)$, a Slater determinant (SD) is a state of the form

$$|\psi_{\mathrm{SD}}(B)\rangle = b_1^\dagger b_2^\dagger \cdots b_\eta^\dagger |\mathbf{0}\rangle , \tag{14}$$

where each $b_i = \sum_{j=1}^n B_{i,j} a_j$ is a sum of annihilation operators in the original basis and the rows of the $\eta \times n$ matrix B are orthonormal.

A. Lowest-energy Slater determinant

Given a local fermionic Hamiltonian in a fixed basis of size n, number η of electrons, and bounds $b > a$, where $b - a = 1/\mathrm{poly}(n)$, determine whether the lowest-energy Slater determinant has energy at most a or at least b. The Slater determinant is specified by the $\eta \times n$ matrix B with entries specified by polynomially many bits.

Theorem 3: (informal). *The lowest-energy Slater determinant problem for electronic-structure Hamiltonians [$H^{(ES)}$ as defined in Eq. (3)] is NP-complete.*

We prove Theorem 3 in Appendix F, building on the proof in Appendix C of Theorem 1, with which it shares many ingredients.

Schuch and Verstraete have shown that the lowest-energy Slater determinant problem for generic quartic number-preserving fermionic Hamiltonians is NP hard [16, arXiv version]. We show NP hardness for the restricted class of such Hamiltonians with coefficients implied by a basis and external potential as in Eqs. (3)–(8); that is, our Theorems 1 and 3 cover the same class of electronic-structure Hamiltonians and differ only in the class of states over which to optimize. Schuch and Verstraete's proof for the QMA hardness of electronic structure with magnetic fields could likely be extended to the NP hardness of the Slater-determinant version, but they have not done so and neither do we.

Slater determinants are useful because they have concise classical descriptions, but they cannot capture the ground states of all electronic-structure Hamiltonians. Two alternative concise classical descriptions of the ground state are the two-body reduced density matrices (2-RDMs) and the electron density. Both contain all the information necessary to compute the energy. However, the determination of whether a given set of 2-RDMs is consistent with a quantum state (known as the N-representability problem) and the actual computation of the energy from the electron density (known as the universal functional in density-functional theory) are both known to be QMA hard under Turing reductions [15,22]. In both cases, it remains an open question whether they remain hard when the inputs are restricted to the ground states of electronic-structure Hamiltonians.

V. CONCLUSIONS AND OPEN PROBLEMS

Our results contribute to a large body of work formally establishing the computational intractability of increasingly physically realistic Hamiltonians. Specifically, we view our hardness results as an important step toward making the abstract framework of computational-complexity theory relevant to the kind of computational problems addressed by practicing chemists. While several aspects of our constructions may seem unnatural, we hope that future work can build on our work to address these issues. As is typical of complexity-theoretic hardness results, ours does not say that *every* instance of the problem considered (i.e., electronic structure in a fixed basis) is hard, but, rather, only that there exist hard instances. Prior to this work, it has been consistent with current knowledge, for example, that merely restricting the Hamiltonian to the form of electronic structure in a fixed basis (with or without an nuclear potential) would make computation of the ground energy tractable; we show conclusively that this is not the case, thereby significantly narrowing the scope of the ongoing search for the boundary between tractable and intractable instances of quantum chemistry. Our result brings the powerful tools of complexity theory to the applied world of quantum chemistry, establishing a strong connection between the two areas that we expect will be the foundation of much more research. For example, it may seem that, based on physical intuition, the rounding of the Hamiltonian done in order to sculpt a Fermi-Hubbard Hamiltonian out of an electronic-structure Hamiltonian is so strong as to preclude the resulting Hamiltonian from capturing electronic correlation. In fact, however, our result means that it can be argued on complexity-theoretic grounds that this in not the case. For if it was not the case that the rounded Hamiltonian captured a significant amount of the corre-

lation energy, then a Slater determinant would suffice to describe its ground state, implying NP = QMA, which is widely believed to be false. That is, because estimating the ground-state energy of the Hamiltonian is QMA hard, if there was always a low-energy Slater determinant that approximates the ground state, then any problem in QMA could be answered (and verified) classically (i.e., it would be in NP). In other words, then any problem in QMA could be solved in NP. We emphasize that this answer exemplifies the value of our work: enabling the power of complexity theory to be applied to electronic-structure problems.

There are still many important problems in computational chemistry the computational complexity of which is unknown. For example, even in a fixed basis, does fixing the spin make the problem easier? Does the problem become more tractable if the given orbitals are guaranteed to have small basis-set error? Is the electronic-structure problem hard in a complete (infinite-dimensional) basis? If so, is it still hard when the external potential arises solely from a set of positively charged nuclei at fixed positions? We pose two variants of the electronic-structure problem the hardness of which is an open question. In both cases, the "size" of the problem is the number of electrons.

A. Electronic structure in a fixed basis with bounded basis-set error

Given an external electric potential V, number of electrons η, thresholds $a < b$, and a basis set $\boldsymbol{\phi}$ with basis-set error $\epsilon(\eta) = 1/\mathsf{poly}(\eta)$ for the given potential V, determine whether the lowest energy of a state in the space spanned by $\boldsymbol{\phi}$ is at most a or greater than $b = a + 1/\mathsf{poly}(\eta)$. The basis-set error is defined as

$$\min_{|\tilde{\psi}\rangle \text{in basis}} \langle\tilde{\psi}|H|\tilde{\psi}\rangle - \min_{|\psi\rangle} \langle\psi|H|\psi\rangle \leq \epsilon(\eta),$$

where both minimizations are over antisymmetric normalized states of η electrons.

The parameters of the *problem* are the promised basis-set error bound $\epsilon(\eta)$, the thresholds $a(\eta)$ and $b(\eta)$, and the family of potentials considered (as a function of η); an instance is specified by simply the number of electrons η, the potential V, and a specification of the basis set $\boldsymbol{\phi}$. This variant entertains the possibility that, while the problem is hard for arbitrary *bases*, it may always be easy for *good* bases (in the sense of having low basis-set error). In practice, chemists always want to use a good basis, and often do, though in general they have no guarantees on the error of the bases that they use. Note that a good basis need not necessarily be complete for the whole space; all that matters is that its span includes a state sufficiently close to the ground state. For example, in Schuch and Verstraete's construction for the QMA hardness of electronic structure with magnetic fields, the external electric potential V implies a good basis of size $n = \eta$ that captures the ground state but is far from complete. Theoretical and numerical results suggest that for physically realistic external potentials there is a always good basis of size $\mathsf{poly}(\eta)$ [19,23], though the constant prefactors may be impractically large. Furthermore, there may exist pathological external potentials for which no polynomially large good basis exists.

To account for both the possibility of no good polynomially large basis and the desirability of working in a small basis, we define another variant of the problem that includes finding the basis in which the state is expressed. The formulation attempts to be as general as possible while remaining in QMA. Ideally, we would like to consider all states that can be efficiently represented and the energy of which can be efficiently estimated by a quantum computer. To formalize this, we specify some family of parametrized orbitals in which the putative low-energy state can be expressed. For example, the family of bases could consist of all weighted sums of Gaussians. In this case, the prover would provide, for each basis element, the centers, the weights, and the exponents of the constituent Gaussians.

B. Electronic structure in parametrized basis

Given an external electric potential V, number of electrons η, thresholds $a < b$, and a family of basis functions $\{\phi_\theta\}_\theta$, and basis size k, determine whether there exists a basis $\boldsymbol{\phi} = (\phi_{\theta_1}, \ldots, \phi_{\theta_k})$ such that the lowest energy of a state in the space spanned by $\boldsymbol{\phi}$ is at most a or greater than $b = a + 1/\mathsf{poly}(\eta)$.

The problem is parametrized by the thresholds $a(\eta)$ and $b(\eta)$ and the family of basis functions $\{\phi_\theta\}_\theta$ allowed; an instance is specified by just the number of electrons η, basis set size k, and potential V. A certificate consists of the classical description of orbitals $\boldsymbol{\phi}$ and a quantum state on $2k$ qubits that is supposed to represent a low-energy of state of η electrons in the basis $\boldsymbol{\phi}$.

ACKNOWLEDGMENTS

We are grateful to the Simons Institute for the Theory of Computing, at whose program on the "The Quantum Wave in Computing" this collaboration began. We thank the anonymous reviewers whose feedback greatly improved the content and presentation of the manuscript. We also acknowledge support from the National Science Foundation (NSF) Quantum Leap Challenge Institute program through Grant No. OMA-2016245. B.O. is supported by a National Aeronautics and Space Administration (NASA) Space Technology Research Fellowship. B.F. acknowledges support from the Air Force Office of Scientific Research (AFOSR) (YIP No. FA9550-18-1-0148 and No. FA9550-21-1-0008). This material is based upon work

partially supported by the NSF under Grant No. CCF-2044923 (CAREER). J.D.W. is supported by funded by the NSF (Grant No. PHYS-1820747) and the U.S. Department of Energy (Grant No. DE-SC0019374). J.D.W. is also supported by NSF (EPSCoR-1921199) and by the U.S. Department of Energy, Office of Science, Office of Advanced Scientific Computing Research under programs Quantum Computing Application Teams and Accelerated Research for Quantum Computing program.

APPENDIX A: OUTLINE OF THE SUPPLEMENTAL MATERIAL

Appendix B gives the reduction from the antiferromagnetic Heisenberg Hamiltonian to the Fermi-Hubbard Hamiltonian, thereby proving Theorem 2. Theorem 1 is proven first without an external potential in Appendix C, using a reduction from Fermi-Hubbard to the electronic-structure Hamiltonian in a fixed basis; Appendix D extends this to include an external nuclear potential in Corollary 1. The proof of Theorem 1 uses a technical lemma, Lemma 1, the proof of which is deferred to Appendix E. Finally, Appendix F shows that finding the lowest-energy Hartree-Fock state for the electronic-structure Hamiltonian in a fixed basis is NP-complete.

The various quantities used in the constructions are summarized in Table II.

1. A note on notation

By $[n]$, we mean the set $\{1, 2, \ldots, n\}$. We use $\|\cdot\|$ for the spectral norm of a matrix and the Euclidean norm of a vector. We use $|\cdot|$ for the element-wise scalar norm.

TABLE II. The quantities used in the constructions.

Quantity	Description	Definition	Related
$H^{(\mathrm{Hubb})}$	Fermi-Hubbard Hamiltonian	Eq. (B1)	$u_0^{(\mathrm{Hubb})}$, $t_{i,j}^{(\mathrm{Hubb})}$
$H^{(\mathrm{Heis})}$	Heisenberg Hamiltonian	Eq. (B2)	$\kappa_{i,j}$
$H^{(\mathrm{ES})}$	Electronic-structure Hamiltonian	Eq. (C1)	
$\xi_\alpha(\mathbf{r})$	Normalized 3D Gaussian	Eq. (C3)	
$\phi_{i,p}(\mathbf{r})$	Primitive orbital	Eq. (C4)	
$\phi_i(\mathbf{r})$	Composite orbital	Eq. (C5)	
c_T	Constant in kinetic operator	Eq. (C31)	
$\omega_{i,j}$	$\alpha\gamma_{i,j}^2$	Eq. (C33)	
$f(\omega)$	$\omega^2 \exp(-\omega)$	Eq. (C33)	
$H^{(\mathrm{round})}$	Rounded Hamiltonian	Eq. (C47)	
$H^{(\mathrm{main})}$	Fermi-Hubbard-like Hamiltonian	Eq. (C48)	
c_U	Constant in electron-electron interaction operator	Eq. (C40)	

APPENDIX B: FERMI-HUBBARD MODEL

We show that the version of the Fermi-Hubbard Hamiltonian problem described below is QMA-complete. In order for the Fermi-Hubbard model to approximate the antiferromagnetic Heisenberg from which we are reducing, we need a large on-site-repulsion term u_0 to penalize orbitals with double occupancy. The Fermi-Hubbard problem remains QMA-complete for any u_0 that satisfies the lower bound in the theorem stated below. For the reduction from Fermi-Hubbard to electronic structure, we require that the $t_{i,j}^{(\mathrm{Hubb})}$ coefficients are bounded by a polynomial in n, the number of electrons. The hardness result that we prove establishes that Fermi-Hubbard remains hard, even under that constraint.

Theorem 2: (QMA-completeness of Hubbard Hamiltonian with uniform on-site repulsion). *There exist constants $p > q > 0$ such that for all $u_0^{(\mathrm{Hubb})} \geq n^{14+3p+2q}$, determining to precision n^{-q} the ground-state energy in the n-particle subspace of a Hubbard Hamiltonian*

$$H^{(\mathrm{Hubb})} = u_0^{(\mathrm{Hubb})} \sum_{i\in[n]} n_{i,+1} n_{i,-1} + \sum_{\substack{i<j \\ \sigma\in\{\pm 1\}}} t_{i,j}^{(\mathrm{Hubb})} \left(a_{i,\sigma}^\dagger a_{j,\sigma} + a_{j,\sigma}^\dagger a_{i,\sigma} \right) \tag{B1}$$

subject to $\left| t_{i,j}^{(\mathrm{Hubb})} \right| \leq \sqrt{n^p u_0^{(\mathrm{Hubb})}}$ is QMA-complete.

We now reduce from the antiferromagnetic Heisenberg Hamiltonian problem.

Definition 1: (antiferromagnetic Heisenberg Hamiltonian). An instance of an antiferromagnetic Heisenberg Hamiltonian is defined by an edge-weighted graph $G = (V, E)$ with $\kappa : E \mapsto \mathbb{R}_{\geq 0}$ as

$$H^{(\mathrm{Heis})}(G, w) = \sum_{\{i,j\}\in E} \kappa_{i,j} \left(X_i X_j + Y_i Y_j + Z_i Z_j \right). \tag{B2}$$

We require in our reduction that the coefficients $\kappa_{i,j}$ are bounded by a polynomial in the number of qubits. Although not explicitly stated, the following theorem is proven in Ref. [10].

Theorem 4: (QMA-completeness of antiferromagnetic Heisenberg Hamiltonian [10]). *Finding the ground state of an antiferromagnetic Heisenberg Hamiltonian is QMA-complete even when restricted to families of Hamiltonians in which the coefficients are bounded by a polynomial in the number of qubits.*

To prove Theorem 2, we show that for sufficiently large $u_0^{(\mathrm{Hubb})}$, the Hubbard model approximates an antiferromagnetic Heisenberg model up to second order in perturbation theory.

We treat $U^{(\mathrm{Hubb})} = u_0^{(\mathrm{Hubb})} \sum_i n_{i,+1} n_{i,-1}$ as the penalty term and $T^{(\mathrm{Hubb})} = H^{(\mathrm{Hubb})} - U^{(\mathrm{Hubb})}$ as the perturbation. To convert the fermionic Hamiltonians above to qubit Hamiltonians, we use the Jordan-Wigner transform with the ordering $(1,+1)$, $(1,-1)$, $(2,+1)$, $(2,-1)$, ... For the full Hilbert space $\mathcal{H}$, we use a basis of one qubit per spin orbital. For the ground space $\mathcal{H}_0$ of $U^{(\mathrm{Hubb})}$, we use a basis of one qubit per spatial orbital, the latter spanning the half-filled subspace of the corresponding pair of spin orbitals. We associate the occupancy of the orbitals of spin $+1$ and -1 with the qubit states $|0\rangle$ and $|1\rangle$, respectively. Let Π_0 be the projector onto $\mathcal{H}_0$ and $\Pi_1 = I - \Pi_0$ the projector onto the orthogonal subspace. In $\mathcal{H}_0$, $U^{(\mathrm{Hubb})}$ is zero ($U_0^{(\mathrm{Hubb})} = \Pi_0 U^{(\mathrm{Hubb})} \Pi_0 = 0$), and outside it is at least $u_0^{(\mathrm{Hubb})}$. In the half-filling regime, the ground space of $U^{(\mathrm{Hubb})}$ is spanned by those basis states having exactly one electron in each spatial orbital. In $\mathcal{H}_0$, $T^{(\mathrm{Hubb})}$ vanishes. In the notation below, we use a bit to indicate whether an orbital is filled. For edge $\{i,j\}$, the first two bits correspond to orbitals $\phi_{i,+1}$ and $\phi_{i,-1}$ and the last two bits correspond to $\phi_{j,+1}$ and $\phi_{j,-1}$. So the state $|0110\rangle$ has $\phi_{i,-1}$ and $\phi_{j,+1}$ filled. The "excitation" terms are

$$T_{1,0}^{(\mathrm{Hubb})} = \Pi_1 T^{(\mathrm{Hubb})} \Pi_0 = \sum_{\{i,j\}\in E} (-1)^{j-i-1} t_{i,j}^{(\mathrm{Hubb})} \times \left[(|1100\rangle + |0011\rangle)(\langle 1001| - \langle 0110|) \right]_{i,j}. \tag{B3}$$

With this, using Theorem 5 from Sec. B 1, we obtain

$$\begin{aligned} H^{(\mathrm{eff})} &= -T_{0,1}^{(\mathrm{Hubb})} \left[U_1^{(\mathrm{Hubb})} \right]^{-1} T_{1,0}^{(\mathrm{Hubb})} \\ &= \sum_{\{i,j\}\in E} \frac{2\left(t_{i,j}^{(\mathrm{Hubb})}\right)^2}{u_0^{(\mathrm{Hubb})}} \left(W_{i,j} - 1\right) = c_{\mathrm{eff}} \\ &\quad + \sum_{\{i,j\}\in E} h_{i,j}^{(\mathrm{eff})} W_{i,j}, \end{aligned} \tag{B4}$$

where

$$h_{i,j}^{(\mathrm{eff})} = 2\frac{\left(t_{i,j}^{(\mathrm{Hubb})}\right)^2}{u_0^{(\mathrm{Hubb})}}, \quad c_{\mathrm{eff}} = -\frac{1}{u_0^{(\mathrm{Hubb})}} \sum_{\{i,j\}\in E} \left(t_{i,j}^{(\mathrm{Hubb})}\right)^2. \tag{B5}$$

1. Perturbation theory

We use the following formulation of second-order perturbation theory, adapted from a special case of the more general formulation by Bravyi *et al.* [24].

Theorem 5: (second-order perturbation theory). *Consider a Hamiltonian $H = H^{(\mathrm{pen})} + H^{(\mathrm{pert})}$. Let Π_0 be the projector onto the ground space of $H^{(\mathrm{pen})}$ and $\Pi_1 = 1 - \Pi_0$. Define*

$$H^{(\mathrm{eff})} = +H_0^{(\mathrm{pert})} - H_{0,1}^{(\mathrm{pert})} \left(H^{(\mathrm{pen})}\right)^{-1} H_{1,0}^{(\mathrm{pert})}, \tag{B6}$$

where $A_i = \Pi_i A \Pi_i$ and $A_{i,j} = \Pi_i A \Pi_j$. If $H_0^{(\mathrm{pen})} = 0$ and $H_1^{(\mathrm{pen})} \geq \Delta \geq 2H^{(\mathrm{pert})}$. Then,

$$\left\| H_{\mathrm{low}} - H^{(\mathrm{eff})} \right\| \leq O\left(\frac{\left\| H^{(\mathrm{pert})} \right\|^3}{\Delta^2} \right), \tag{B7}$$

where H_{low} is the projection of H onto its eigenspace with eigenvalues at most $\Delta/2$.

2. Fermi-Hubbard is QMA hard

Proof of Theorem 2. There are constants $p, q \geq 0$ such that it is QMA hard to find the ground-state energy to precision n^{-q} of

$$H^{(\mathrm{Heis})} = \sum_{\{i,j\}\in E} \kappa_{i,j} W_{i,j} \tag{B8}$$

subject to $0 \leq \kappa_{i,j} \leq n^p$. Consider such an instance. We want to choose $u_0^{(\mathrm{Hubb})}$ and $t_{i,j}^{(\mathrm{Hubb})}$ such that

$$H^{(\mathrm{Heis})} = H^{(\mathrm{eff})} - c_{\mathrm{eff}} \tag{B9}$$

and

$$\left\| H_{\mathrm{low}}^{(\mathrm{Hubb})} - H^{(\mathrm{eff})} \right\| = o(n^{-q}). \tag{B10}$$

The first constraint, Eq. (B9), is

$$\kappa_{i,j} = h_{i,j}^{(\mathrm{eff})} = 2\frac{\left(t_{i,j}^{(\mathrm{Hubb})}\right)^2}{u_0^{(\mathrm{Hubb})}} \tag{B11}$$

or

$$t_{i,j}^{(\mathrm{Hubb})} = \pm\sqrt{u_0^{(\mathrm{Hubb})} \kappa_{i,j}/2}. \tag{B12}$$

Therefore, for any $\kappa_{i,j}$ such that $|\kappa_{i,j}| \leq n^p$ we can choose $t_{i,j}^{(\mathrm{Hubb})}$ such that $\left|t_{i,j}^{(\mathrm{Hubb})}\right| \leq \sqrt{n^p u_0^{(\mathrm{Hubb})}}$ and that Eq. (B9) is satisfied. To satisfy the second constraint, Eq. (B10), we use second-order perturbation theory (Theorem 5).

Furthermore, the assumption that $u_0^{(\mathrm{Hubb})} \geq n^{14+3p+2q}$ implies that the condition of Theorem 5 is met:

$$\left\| T^{(\mathrm{Hubb})} \right\| \leq \sum_{\substack{\{i,j\}\in E \\ \sigma\in\{\pm 1\}}} \left| t_{i,j}^{(\mathrm{Hubb})} \right| \tag{B13}$$

$$\leq \underbrace{n^2}_{\{i,j\},\sigma} \times \underbrace{\sqrt{u_0^{(\mathrm{Hubb})} n^p}}_{t_{i,j}^{(\mathrm{Hubb})}} \tag{B14}$$

$$= \sqrt{u_0^{(\mathrm{Hubb})}} \sqrt{n^{4+p}} \tag{B15}$$

$$\leq \sqrt{u_0^{(\mathrm{Hubb})}} \times \frac{1}{2}\sqrt{n^{14+3p+2q}} \quad n \geq 2; p, q \geq 0 \tag{B16}$$

$$\leq \sqrt{u_0^{(\mathrm{Hubb})}} \times \frac{1}{2}\sqrt{u_0^{(\mathrm{Hubb})}} = \frac{1}{2} u_0^{(\mathrm{Hubb})}. \tag{B17}$$

Theorem 5 then yields

$$\left\| H_{\mathrm{low}}^{(\mathrm{Hubb})} - H^{(\mathrm{eff})} \right\| \leq O\left(\frac{\left\| T^{(\mathrm{Hubb})} \right\|^3}{\left(u_0^{(\mathrm{Hubb})} \right)^2} \right)$$

$$\leq O\left(\frac{\overbrace{n^6 n^{1.5p} \left(u_0^{(\mathrm{Hubb})} \right)^{1.5}}^{(\mathrm{B14})}}{\left(u_0^{(\mathrm{Hubb})} \right)^2} \right) \tag{B18}$$

$$= O\left(\frac{n^6 n^{1.5p}}{\sqrt{u_0^{(\mathrm{Hubb})}}} \right) \leq O\left(\frac{n^6 n^{1.5p}}{\sqrt{n^{14+3p+2q}}} \right)$$

$$= O\left(n^{-(q+1)} \right) = o\left(n^{-q} \right). \tag{B19}$$

■

APPENDIX C: ELECTRONIC STRUCTURE

Here, we prove our main result.

Theorem 1: (QMA-completeness of electronic structure in fixed basis). *Determination of the ground-state energy of an electronic-structure Hamiltonian in a fixed basis and with a fixed particle number to inverse-polynomial precision is QMA-complete.*

For ease of presentation, we first prove the theorem using Hamiltonians with no external potential. In Appendix D, we show how the proof holds even when including a "nuclear" potential (i.e., that due to positive point charges at fixed positions); essentially, we can choose the nuclear positions such that, within the fixed basis and at a fixed particle number, the nuclei contribute to the overall energy an additive constant plus some corrections that are negligible compared to the other parts of the Hamiltonian.

We start by defining a set of n spatial orbitals. Once the orbitals are fixed, the t and u coefficients are determined by the integrals in Eqs. (6) and (8), which then yields the physical Hamiltonian

$$H^{(\mathrm{ES})} = T + U = \sum_{\substack{i,j\in[n] \\ \sigma\in\{\pm 1\}}} t_{i,j} a_{i,\sigma}^\dagger a_{j,\sigma} + \frac{1}{2} \sum_{\substack{i,j,k,l\in[n] \\ \sigma,\tau\in\{\pm 1\}}} u_{i,j,k,l} a_{i,\sigma}^\dagger a_{j,\tau}^\dagger a_{k,\tau} a_{l,\sigma} \tag{C1}$$

in the absence of any external potential ($V = 0$). We show that, when restricted to the subspace with exactly n electrons (with arbitrary spin), this yields an effective Hamiltonian that is close, up to rescaling and shifting, to a Fermi-Hubbard Hamiltonian

$$H^{(\mathrm{Hubb})} = u_0^{(\mathrm{Hubb})} \sum_{i\in[n]} n_{i,+1} n_{i,-1} + \sum_{i<j} t_{i,j}^{(\mathrm{Hubb})} \left(a_{i,\sigma}^\dagger a_{j,\sigma} + a_{j,\sigma}^\dagger a_{i,\sigma} \right) \tag{C2}$$

with constants $p > q > 0$ such that $u_0^{(\mathrm{Hubb})} \geq n^{14+3p+2q}$ and $\left| t_{i,j}^{(\mathrm{Hubb})} \right| \leq \sqrt{n^p u_0^{(\mathrm{Hubb})}}$ for all edges $\{i,j\}$.

1. Orbitals

Recall from Sec. III B that our goal is a basis of orbitals such that the electronic structure Hamiltonian in that basis is sufficiently close to a Hubbard Hamiltonian. We define here a set of orbitals that effectively encodes the interaction graph of the Hubbard Hamiltonian. Each orbital represents a vertex of the interaction graph and consists of a superposition of Gaussians centered at various points in space. For the most part, these Gaussians are far apart from each other. If two vertices are connected by an edge, then their corresponding orbitals have two Gaussians that are relatively close to each other. This distance between the Gaussians can be tuned to match the interaction coefficient in the Hubbard Hamiltonian. Let

$$\xi_\alpha(\mathbf{r}) = \left(\frac{2\alpha}{\pi} \right)^{3/4} \exp\left(-\alpha \|\mathbf{r}\|^2 \right) \tag{C3}$$

be the Gaussian centered at $\mathbf{0} \in \mathbb{R}^3$ with exponent $\alpha > 0$. Each of our orbitals is a superposition of Gaussians. The centers of these Gaussians comprise a set of points $\{\mathbf{x}_{i,l}\}_{i,l}$ in $\mathbb{R}^3$, where $i \in [n]$ and $l \in \{0\} \cup [d]$, and $d \leq n-1$ is an upper bound on the maximum degree of the interaction graph G. Note that although the points are in $\mathbb{R}^3$, the properties we require of them can be satisfied by placing them all along a line; Fig. 1 illustrates the construction with

a small example. We require two properties of this set of points:

(1) For each edge $\{i,j\}$ in the interaction graph, there is exactly one pair $(l,l') \in [d]^2$ such that $\left\|\mathbf{x}_{i,l} - \mathbf{x}_{j,l'}\right\| = \gamma_{i,j} > 0$. Let $\gamma_{\min}$ and $\gamma_{\max}$ be lower and upper bounds on $\gamma_{i,j}$ over $\{i,j\} \in E$.
(2) Every other pair of points is at least $\Gamma \gg \gamma_{\max}$ apart (in Euclidean distance).

The important part is the $m = |E|$ pairs of points such that points from different pairs are at least a distance of Γ apart. Each pair of points is associated with an edge $\{i,j\}$ in the interaction graph. The pair of points associated with edge $\{i,j\}$ is $\gamma_{i,j}$ apart, where $\Gamma \gg \gamma_{i,j}$. In addition, there is a set X of $(d+1)n - 2m$ points each of which is a distance at least Γ from any other point in the construction. The points associated with vertex i in the interaction graph are as follows:

(1) $x_{i,0}$ is a point from X.
(2) If $p \leq \deg(i)$ and j is the pth neighbor of vertex i, then $x_{i,p}$ is one of the points from the pair associated with edge $\{i,j\}$. (The other point from the pair belongs to vertex j.)
(3) If $p > \deg(i)$, then $x_{i,p}$ is a point from X. (These are just dummy neighbors to ensure that all of the orbitals have the same form.)

With these points, we can define the *primitive* orbitals:

$$\phi_{i,p}(\mathbf{r}) = \begin{cases} \xi_\beta\left(\mathbf{r} - \mathbf{x}_{i,0}\right), & p = 0, \\ \xi_\alpha\left(\mathbf{r} - \mathbf{x}_{i,p}\right), & \text{otherwise}, \end{cases} \tag{C4}$$

where α and β are positive constants to be set later. Ultimately, we need $\beta \gg \alpha$. The *composite* orbitals that we use in the construction are superpositions of these primitive orbitals:

$$\phi_i(\mathbf{r}) = \frac{1}{\sqrt{2}}\phi_{i,0}(\mathbf{r}) + \frac{1}{\sqrt{2d}}\sum_{l=1}^{d}\phi_{i,l}(\mathbf{r}). \tag{C5}$$

It is convenient to be able to refer to the indices of the primitive orbitals that are a distance $\gamma_{i,j}$ apart, corresponding to edge $\{i,j\}$. Define $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$, where j is the pth neighbor of i and i is the qth neighbor of j.

We eventually show that the kinetic energy terms between the primitive orbitals that are separated by only a distance of $\gamma_{i,j}$ are the dominant terms in the Hamiltonian (besides the on-site repulsion). We then tune the $\gamma_{i,j}$ distances so that the coefficients resulting from kinetic energy integrals scale with the $t_{i,j}^{(\mathrm{Hubb})}$ from Eq. (C2), which are the coefficients in the Fermi-Hubbard Hamiltonian from which we are reducing. The radius β is chosen to be large enough so that the potential-energy coefficients $u_{i,i,i,i}$ effectively result in a $u_0 n_{i,+1} n_{i,-1}$ with a large coefficient u_0.

The orbitals are strictly positive everywhere, so the overlap $\int d\mathbf{r}\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$ cannot be exactly zero, but we show that it is very close. That is, we show that the orbitals are not perfectly orthonormal but that they are sufficiently close. For now, we proceed as if they are and address the effect of the nonorthonormality in Sec. C 2. The purpose of including the $\phi_{i,0}$ component as part of the orbital, which is far away from every other primitive orbital center, is to decouple the scale of the on-site-repulsion term in the Hamiltonian from that of the interaction term, which is effected by the one of the components $\left\{\phi_{i,l}\right\}_{1\leq\deg(i)}$. To this end, we ultimately set $\beta \gg \alpha$. Including the other components $\left\{\phi_{i,l'}\right\}_{l'>\deg(i)}$ is simply to ease the analysis by making all of the orbitals $\{\phi_i\}_i$ have integrals, over single-electron operators, that are of approximately the same form.

a. Integrals of operators over Gaussians

Since the composite orbitals are superpositions of primitive orbitals, the expressions for overlap, kinetic energy, and potential energy for the composite orbitals are linear combinations of the corresponding expression for combinations of primitive orbitals. The following integrals of operators over Gaussians are useful in expressing these terms for the primitive orbitals.

The overlap of two Gaussians with exponents α and β with centers $\mathbf{x}$ apart:

$$\begin{aligned} s_{\alpha,\beta}(\|\mathbf{x}\|) &= \int d\mathbf{r}\xi_\alpha(\mathbf{r})\xi_\beta(\mathbf{r}-\mathbf{x}) \\ &= \left(\frac{2\sqrt{\alpha\beta}}{\alpha+\beta}\right)^{3/2}\exp\left(-\frac{\alpha\beta}{\alpha+\beta}\|\mathbf{x}\|^2\right). \end{aligned} \tag{C6}$$

Due to the rotational invariance of the Gaussians, all of the functions defined in this subsection depend only on the magnitude of their argument and so we write, for example, $s(\|\mathbf{x}\|)$.

We can define the $n(d+1) \times n(d+1)$ matrix S of overlap between the primitive orbitals, where each row and column is indexed by a pair (i,p) corresponding to a primitive orbital:

$$s_{(i,p),(j,q)} = -\frac{1}{2}\int d\mathbf{r}\phi^*_{(i,p)}(\mathbf{r})\phi_{(j,q)}(\mathbf{r}). \tag{C7}$$

Note that $s_{\alpha,\beta}(\|\mathbf{x}\|)$ denotes the overlap of primitive orbital $\phi_{i,0}$ (the exponent of which is β) and $\phi_{j,p>0}$ (the exponent of which is α), where $\phi_{i,0}$ and $\phi_{j,p}$ are separated by a distance $\|\mathbf{x}\|$: $s_{(i,0),(j,p)} = s_{\alpha,\beta}(\|\mathbf{x}\|)$. The overlap of two primitive orbitals with the same exponent is denoted

by

$$s_\alpha(\|\mathbf{x}\|) = s_{\alpha,\alpha}(\|\mathbf{x}\|) = \exp\left(-\alpha\|\mathbf{x}\|^2/2\right), \tag{C8}$$

$$s_\beta(\|\mathbf{x}\|) = s_{\beta,\beta}(\|\mathbf{x}\|) = \exp\left(-\beta\|\mathbf{x}\|^2/2\right). \tag{C9}$$

Therefore, $s_{(i,0),(j,0)} = s_\beta(\|\mathbf{x}\|)$, where primitive orbitals $\phi_{(i,0)}$ and $\phi_{(j,0)}$ are a distance $\|\mathbf{x}\|$ apart. Also, $s_{(i,p),(j,q)} = s_\alpha(\|\mathbf{x}\|)$, where $p,q>0$ and primitive orbitals $\phi_{(i,p)}$ and $\phi_{(j,q)}$ are a distance $\|\mathbf{x}\|$ apart.

The kinetic energy between two Gaussians with exponents α and β with centers $\mathbf{x}$ apart is as follows:

$$\begin{aligned} t_{\alpha,\beta}(\|\mathbf{x}\|) &= -\frac{1}{2}\int d\mathbf{r}\xi_\alpha(\mathbf{r})\nabla^2\xi_\beta(\mathbf{r}-\mathbf{x}) \\ &= 2^{3/2}\frac{(\alpha\beta)^{7/4}}{(\alpha+\beta)^{5/2}}\left(3-2\mu\|\mathbf{x}\|^2\right)\exp\left(-\mu\|\mathbf{x}\|^2\right) \\ &\le \frac{3}{2}\max\{\alpha,\beta\}, \end{aligned} \tag{C10}$$

where $\mu = \alpha\beta/(\alpha+\beta)$, with

$$t_\alpha(\|\mathbf{x}\|) = t_{\alpha,\alpha}(\|\mathbf{x}\|) = \frac{\alpha}{2}\left(3-\alpha\|\mathbf{x}\|^2\right)\exp\left(-\alpha\|\mathbf{x}\|^2/2\right), \tag{C11}$$

$$t_\beta(\|\mathbf{x}\|) = t_{\beta,\beta}(\|\mathbf{x}\|) = \frac{\beta}{2}\left(3-\beta\|\mathbf{x}\|^2\right)\exp\left(-\beta\|\mathbf{x}\|^2/2\right). \tag{C12}$$

Define T to be the $n(d+1)\times n(d+1)$ matrix of kinetic energy terms between primitive orbitals. An entry of matrix T is

$$t_{(i,p),(j,q)} = -\frac{1}{2}\int d\mathbf{r}\phi^*_{(i,p)}(\mathbf{r})\nabla^2\phi_{(j,q)}(\mathbf{r}). \tag{C13}$$

Therefore, $t_{(i,0),(j,0)} = t_\beta(\|\mathbf{x}\|)$, where primitive orbitals $\phi_{(i,0)}$ and $\phi_{(j,0)}$ are a distance $\|\mathbf{x}\|$ apart. Also, $t_{(i,p),(j,q)} = t_\alpha(\|\mathbf{x}\|)$, where $p,q>0$ and primitive orbitals $\phi_{(i,p)}$ and $\phi_{(j,q)}$ are a distance $\|\mathbf{x}\|$ apart.

The potential integrals are as follows:

$$\begin{aligned} u^{(\mathrm{Coul})}_\alpha(\|\mathbf{x}\|) &= \int d\mathbf{r}d\mathbf{s}\xi_\alpha(\mathbf{r})^2\xi_\alpha(\mathbf{s}-\mathbf{x})^2\|\mathbf{r}-\mathbf{s}\|^{-1} \\ &= \sqrt{\frac{4\alpha}{\pi}}F_0\left(\alpha\|\mathbf{x}\|^2\right) \le 2\sqrt{\alpha}, \end{aligned} \tag{C14}$$

$$\begin{aligned} u^{(\mathrm{exch})}_\alpha(\|\mathbf{x}\|) &= \int d\mathbf{r}d\mathbf{s}\xi_\alpha(\mathbf{r})\xi_\alpha(\mathbf{r}-\mathbf{x})\xi_\alpha(\mathbf{s})\xi_\alpha(\mathbf{s}-\mathbf{x}) \\ &\quad\times\|\mathbf{r}-\mathbf{s}\|^{-1} = \exp\left(-\alpha\|\mathbf{x}\|^2\right)u^{(\mathrm{Coul})}_\alpha(0), \end{aligned} \tag{C15}$$

$$\begin{aligned} u^{(\mathrm{other})}_\alpha(\|\mathbf{x}\|) &= \int d\mathbf{r}d\mathbf{s}\xi_\alpha(\mathbf{r})^2\xi_\alpha(\mathbf{s})\xi_\alpha(\mathbf{s}-\mathbf{x})\|\mathbf{r}-\mathbf{s}\|^{-1} \\ &= \exp\left(-\alpha\|\mathbf{x}\|^2/2\right)u^{(\mathrm{Coul})}_\alpha(\mathbf{x}/2), \end{aligned} \tag{C16}$$

where

$$F_k(x) = \int_0^1 e^{-xt^2}t^{2k}dt \tag{C17}$$

is the Boys function of order k. The analogous definitions for $u^{(\mathrm{other})}_\beta(\mathbf{x})$, $u^{(\mathrm{other})}_\beta(\mathbf{x})$, and $u^{(\mathrm{other})}_\beta(\mathbf{x})$ use Gaussians with exponent β. The potential-energy terms on the primitive orbitals are represented by an $n^2(d+1)^2\times n^2(d+1)^2$ matrix U, where each row and column is indexed by a pair of primitive orbitals $[(i,p),(j,q)]$. The entry in row $[(i,p),(j,q)]$ and column $[(k,r),(l,s)]$ is the potential-energy term for orbitals $\phi_{(i,p)}(\mathbf{r})$, $\phi_{(j,q)}(\mathbf{r})$, $\phi_{(k,r)}(\mathbf{r})$, and $\phi_{(l,s)}(\mathbf{r})$:

$$\begin{aligned} &u_{[(i,p),(j,q)],[(k,r),(l,s)]} \\ &\quad= \int d\mathbf{r}d\mathbf{s}\frac{\phi^*_{(i,p)}(\mathbf{r})\phi^*_{(j,q)}(\mathbf{s})\phi_{(k,r)}(\mathbf{s})\phi_{(l,s)}(\mathbf{r})}{|\mathbf{r}-\mathbf{s}|}. \end{aligned} \tag{C18}$$

The definitions of the integral functions above correspond to the situation where all four indices (i,p), (j,q), (k,r), and (l,s) denote at most two distinct orbitals with the same exponent. Specifically, for $p,q>0$, where $\|\mathbf{x}\|$ is the distance between $\phi_{(i,p)}$ and $\phi_{(j,q)}$,

$$u_{[(i,p),(j,q)],[(j,q),(i,p)]} = u^{(\mathrm{Coul})}_\alpha(\mathbf{x}), \tag{C19}$$

$$u_{[(i,p),(j,q)],[(i,p),(j,q)]} = u^{(\mathrm{exch})}_\alpha(\mathbf{x}), \tag{C20}$$

$$u_{[(i,p),(i,p)],[(i,p),(j,q)]} = u^{(\mathrm{other})}_\alpha(\mathbf{x}). \tag{C21}$$

2. Orthonormalizing and rounding

Having constructed our orbitals, we now make two approximations to get a clean "round" Hamiltonian $H^{(\mathrm{round})}$. First, the orbitals we define in Eq. (C5) are slightly nonorthonormal, and so we derive a related orthonormalized basis in which the electronic-structure Hamiltonian does not change too much. Second, we remove contributions to the Hamiltonian from the electron-electron interaction pairs of primitive orbitals that are far ($>\Gamma$) away from each other. The error of these approximations is quantified by Lemma 1.

The matrix S is defined in Eq. (C7) to be the overlap matrix of the *primitive* orbitals. We can construct a set of orthonormal primitive orbitals by setting

$$\tilde{\phi}_{i,k}(\mathbf{r}) = \sum_{j,l}\left[S^{-1/2}\right]_{(j,l),(i,k)}\phi_{j,l}(\mathbf{r}) \tag{C22}$$

and new orthonormal composite orbitals

$$\tilde{\phi}_i(\mathbf{r}) = \frac{1}{\sqrt{2}}\tilde{\phi}_{i,0}(\mathbf{r}) + \frac{1}{\sqrt{2d}}\sum_{l=1}^{d}\tilde{\phi}_{i,l}(\mathbf{r}) \tag{C23}$$

with annihilation operators $\tilde{a}_{i,\sigma}$ [2]. The Hamiltonian in this orthonormal basis is

$$H^{(\mathrm{ES})} = T^{(\mathrm{ES})} + U^{(\mathrm{ES})} = \sum_{\substack{i,j\in[n]\\ \sigma\in\{\pm1\}}} \tilde{t}_{i,j}\tilde{a}^{\dagger}_{i,\sigma}\tilde{a}_{j,\sigma} + \frac{1}{2}\sum_{\substack{i,j,k,l\in[n]\\ \sigma,\tau\in\{\pm1\}}} \tilde{u}_{i,j,k,l}\tilde{a}^{\dagger}_{i,\sigma}\tilde{a}^{\dagger}_{j,\tau}\tilde{a}_{k,\tau}\tilde{a}_{l,\sigma}, \tag{C24}$$

where

$$\tilde{t}_{i,j} = \int d\mathbf{r}\tilde{\phi}^{*}_{i}(\mathbf{r})T\tilde{\phi}_{j}(\mathbf{r}), \tag{C25}$$

$$\tilde{u}_{i,j,k,l} = \int d\mathbf{r}d\mathbf{s}\tilde{\phi}^{*}_{i}(\mathbf{r})\tilde{\phi}^{*}_{j}(\mathbf{s})U\tilde{\phi}_{k}(\mathbf{s})\tilde{\phi}_{l}(\mathbf{r}). \tag{C26}$$

The matrices $\tilde{T}$ and $\tilde{U}$ showing the kinetic and potential energies using the orthonormalized primitive orbitals are analogous to the definitions given in Eqs. (C13) and (C18). The pair T and $\tilde{T}$ and the pair U and $\tilde{U}$ are related by conjugation by $S^{-1/2}$:

$$\tilde{T} = S^{-1/2}\,T\,S^{-1/2}, \tag{C27}$$

$$\tilde{U} = (S^{-1/2}\otimes S^{-1/2})\,U\,(S^{-1/2}\otimes S^{-1/2}). \tag{C28}$$

Since $S\approx I$, the coefficients $\tilde{t}$ and $\tilde{u}$ for the orthonormalized orbitals are close to t and u for the nonorthonormalized orbitals but the difference needs to be carefully bounded. We approximate $H^{(\mathrm{ES})}$ by the Hamiltonian $H^{(\mathrm{round})}$ that uses creation and annihilation operators of the orthonormal basis $\tilde{\boldsymbol{\phi}}$ with the original coefficients, subject to two modifications. First, we add a first-order correction to the off-diagonal kinetic coefficients. Second, we remove contributions from pairs of primitive orbitals that are at least Γ apart (which makes many terms vanish completely).

The rounded Hamiltonian is

$$H^{(\mathrm{round})} = T^{(\mathrm{round})} + U^{(\mathrm{round})}. \tag{C29}$$

The rounded kinetic operator is

$$T^{(\mathrm{round})} = t^{(\mathrm{round})}_{i,i}\sum_{\substack{i\in[n]\\ \sigma\in\{\pm1\}}}\tilde{n}_{i,\sigma} + \sum_{\substack{\{i,j\}\in E\\ \sigma\in\{\pm1\}}} t^{(\mathrm{round})}_{i,j}\left(\tilde{a}^{\dagger}_{i,\sigma}\tilde{a}_{j,\sigma} + \tilde{a}^{\dagger}_{j,\sigma}\tilde{a}_{i,\sigma}\right), \tag{C30}$$

$$t^{(\mathrm{round})}_{i,i} = c_T = \frac{1}{2}\left[t_\alpha(0) + t_\beta(0)\right], \tag{C31}$$

$$t^{(\mathrm{round})}_{i,j} = -\frac{\alpha}{4d}\sqrt{f(\omega_{i,j})}, \tag{C32}$$

where

$$\omega_{i,j} = \alpha\gamma^{2}_{i,j}, \quad f(\omega) = \omega^{2}\exp(-\omega). \tag{C33}$$

Before getting to the rounded potential operator, let us consider the difference between $T^{(\mathrm{round})}$ and the true kinetic operator $T^{(\mathrm{ES})}$ in Eq. (C24). Let $\psi_0 = 1/\sqrt{2}$ and $\psi_l = 1/\sqrt{2d}$ for $l > 0$. Since the composite orbitals are superpositions of the primitive orbitals, the kinetic energy term for a pair of composite orbitals is just a linear combination of kinetic energy terms for pairs of primitive orbitals:

$$\tilde{t}_{i,j} = \sum_{p,q}\psi_p\psi_q\tilde{t}_{(i,p),(j,q)}. \tag{C34}$$

We eventually show that the kinetic energy contribution for pairs of primitive orbitals that are at least Γ apart are negligible. Therefore, the only kinetic energy terms that contribute significantly to the sum above are $\tilde{t}_{(i,p),(i,p)}$ and $\tilde{t}_{(i,p),(j,q)}$, where $\{i,j\}$ is an edge and $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$. This means that for edge $\{i,j\}$, there is only one significant term in the sum for $\tilde{t}_{i,j}$. If $\{i,j\}$ is not an edge, then all of the primitive orbitals for composite orbitals i and j are at least Γ apart, and $\tilde{t}_{i,j}\approx 0$. For the diagonal terms $\tilde{t}_{i,i}$, there are $d+1$ significant terms in the sum, corresponding to $\tilde{t}_{(i,p),(i,p)}$ terms. Thus, we show that

$$\tilde{t}_{i,j} = \sum_{p,q}\psi_p\psi_q\tilde{t}_{(i,p),(j,q)} \approx \begin{cases} \sum_{p}\psi^{2}_{p}\tilde{t}_{(i,p),(i,p)}, & i=j,\\ \dfrac{1}{2d}\tilde{t}_{(i,p),(j,q)}, & \{i,j\}\in E,\\ 0, & \{i,j\}\notin E, \end{cases} \tag{C35}$$

where $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$. We would now like to approximate each $\tilde{t}_{(i,p),(j,q)}$ with $t_{(i,p),(j,q)}$, which is the kinetic energy term for a pair of simple Gaussians. This turns out to be a sufficiently accurate approximation for $\tilde{t}_{(i,p),(i,p)}$. Note that

$$t^{(\mathrm{round})}_{i,i} = \frac{1}{2}\left[t_\alpha(0) + t_\beta(0)\right] = \sum_{p}\psi^{2}_{p}t_{(i,p),(i,p)}.$$

However, for edge $\{i,j\}$, where $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$, primitive orbitals $\phi_{(i,p)}$ and $\phi_{(j,q)}$ are only $\gamma_{i,j}$ apart. In this case, there is sufficient overlap between the orbitals that the effect of orthonormalizing the orbitals has a significant impact on the kinetic energy between the pair. Therefore, instead of setting $t^{(\mathrm{round})}_{i,j}$ to be $(1/2d)t_{(i,p),(j,q)}$, we use a slightly corrected expression as defined by the function f.

For comparison,

$$\frac{1}{2d}t_{(i,p),(j,q)} = \frac{\alpha}{4d}(3-\omega_{i,j})\exp(-\omega_{i,j}/2), \tag{C36}$$

$$t_{i,j}^{(\mathrm{round})} = -\frac{\alpha}{4d}\sqrt{f(\omega_{i,j})} = \frac{-\alpha\omega_{i,j}}{4d}\exp(-\omega_{i,j}/2). \tag{C37}$$

For the potential operator, the coefficients u are a sufficiently good approximation for the $\tilde{u}$. We show that we can also drop potential-energy terms that involve any two primitive orbitals that are a distance at least Γ apart. Thus, we only need to include terms $u_{[(i,p),(j,q)],[(k,r),(l,s)]}$, where the indices (i,p), (j,q), (k,r), and (l,s) are all the same or all come from the set $\mathcal{B}(i,j)$ for some edge $\{i,j\}$. Thus, $u_{i,j,k,l}^{(\mathrm{round})}$ are 0, except when i,j,k,l are all equal or are all endpoints of the same edge. The rounded potential operator is

$$U^{(\mathrm{round})} = \frac{1}{2}\sum_{\substack{(i,j,k,l)\in B\\ \sigma\in\pm 1}} u_{i,j,k,l}^{(\mathrm{round})}\tilde{a}_{i,\sigma}^{\dagger}\tilde{a}_{j,\tau}^{\dagger}\tilde{a}_{k,\tau}\tilde{a}_{l,\sigma}, \tag{C38}$$

where

$$B = \bigcup_{\{i,j\}\in E}\{i,j\}^4 \tag{C39}$$

is the set of all 4-tuples of indices such that they are all the same or there are two distinct indices corresponding to an edge in the graph. For example, $(i,i,i,i),(i,j,j,i)\in B$ but $(i,i,j,k),(i,k,k,i)\notin B$ for $\{i,j\}\in E$ and $\{i,k\}\notin E$. The coefficients are defined as follows:

$$c_U^{(\mathrm{round})} = u_{i,i,i,i}^{(\mathrm{round})} = \frac{1}{4}u_{(i,0),(i,0),(i,0),(i,0)} + \frac{1}{4d^2}\sum_{p\in[d]} u_{(i,p),(i,p),(i,p),(i,p)} \tag{C40}$$

$$= \frac{1}{4}u_{\beta}^{(\mathrm{Coul})}(0) + \frac{1}{4d}u_{\alpha}^{(\mathrm{Coul})}(0), \tag{C41}$$

$$u_{i,j,j,i}^{(\mathrm{round})} = u_{j,i,i,j}^{(\mathrm{round})} = \frac{1}{4d^2}u_{(i,p),(j,q),(j,q),(i,p)} = \frac{1}{4d^2}u_{\alpha}^{(\mathrm{Coul})}(\gamma_{i,j}), \tag{C42}$$

$$u_{i,i,j,j}^{(\mathrm{round})} = u_{j,j,i,i}^{(\mathrm{round})} = u_{i,j,i,j}^{(\mathrm{round})} = u_{j,i,j,i}^{(\mathrm{round})} = \frac{1}{4d^2}u_{(i,p),(i,p),(j,q),(j,q)} = \frac{1}{4d^2}u_{\alpha}^{(\mathrm{exch})}(\gamma_{i,j}), \tag{C43}$$

$$u_{i,i,i,j}^{(\mathrm{round})} = u_{i,i,j,i}^{(\mathrm{round})} = u_{i,j,i,i}^{(\mathrm{round})} = u_{j,i,i,i}^{(\mathrm{round})} = u_{j,j,j,i}^{(\mathrm{round})} = u_{j,j,i,j}^{(\mathrm{round})} = u_{j,i,j,j}^{(\mathrm{round})} = u_{i,j,j,j}^{(\mathrm{round})} = \frac{1}{4d^2}u_{(i,p),(i,p),(i,p),(j,q)} = \frac{1}{4d^2}u_{\alpha}^{(\mathrm{other})}(\gamma_{i,j}), \tag{C44, C45}$$

with $u_{i,j,k,l}^{(\mathrm{round})} = 0$ for $(i,j,k,l)\notin B$. The following lemma bounds the difference between $H^{(\mathrm{ES})}$ and $H^{(\mathrm{round})}$.

Lemma 1: *If* $\beta\geq\alpha\geq 1$, $\omega_{\min}\geq 4$, $\Gamma\geq 640n^{18}\beta^3$, *and* $\alpha\Gamma^2\geq 12\log\beta+80\log n+4\omega_{\min}+24$, *then*

$$\left\|H^{(ES)}-H^{(round)}\right\| \leq 3n^2\alpha f(\omega_{\min}) + \frac{1}{20n^2} + 8n^4\sqrt{\alpha}\exp(-\omega_{\min}/2), \tag{C46}$$

where $\omega_{\min}=\alpha\gamma_{\min}^2$.

The matrices T, $\tilde{T}$, S, and $S^{-1/2}$ are all close to block diagonal. Blocks are either single entries on the diagonal (corresponding to primitive orbitals that are a distance at least Γ from all other primitive orbitals) or a 2×2 submatrix corresponding to an edge $\{i,j\}$. Suppose that $\mathcal{B}(i,j)=\{(i,p),(j,q)\}$. For any $n(d+1)\times n(d+1)$ matrix A, let $A_{i,j}$ denote the 2×2 submatrix of A indexed by the elements of $\mathcal{B}(i,j)$:

$$A_{i,j} = \begin{pmatrix} a_{(i,p),(i,p)} & a_{(i,p),(j,q)} \\ a_{(j,q),(i,p)} & a_{(j,q),(j,q)} \end{pmatrix}.$$

We refer to all of the $A_{i,j}$ blocks collectively as the *edge blocks* of A. The proof of Lemma 1 uses the fact that the off-diagonal terms of T outside of the $T_{i,j}$ blocks are small. The same is true for $\tilde{T}$ and $R=S^{-1/2}$.

$\tilde{U}$ and U are also related by conjugation by $S^{-1/2}\otimes S^{-1/2}$. We show that $\tilde{U}$ and U are also close to block diagonal. We define $U_{i,j}$ to be the 4×4 submatrix of U corresponding to the intersections of the four rows and four columns indexed by

$$[(i,p),(i,p)],\ [(i,p),(j,q)],\ [(j,q),(i,p)],\ [(j,q),(j,q)].$$

The proof of Lemma 1 uses the fact that the off-diagonal terms of U outside of the $U_{i,j}$ blocks are small. The same is true for $\tilde{U}$. We refer to all of the $U_{i,j}$ blocks collectively as the *edge blocks*.

Lemma 1 is proved in Appendix E. Outside of this subsection, all creation and annihilation operators are those of the orthonormalized basis $\tilde{\boldsymbol{\phi}}$; in other words, we drop the tildes.

3. Getting the main Hamiltonian

With the rounded Hamiltonian $H^{(\mathrm{round})}$ in hand, we make one final approximation to get to the main Hamiltonian $H^{(\mathrm{main})}$ that we later show is close to a Hubbard Hamiltonian. Specifically, we remove the "off-diagonal" Coulomb interaction terms. The error of this approximation is bounded by Lemma 2.

The main Hamiltonian is

$$H^{(\text{round})} = H^{(\text{main})} + H^{(\text{approx})} + nc_T, \tag{C47}$$

$$H^{(\text{main})} = c_U^{(\text{main})} \sum_i n_{i,+1} n_{i,-1} + \sum_{\substack{\{i,j\}\in E \\ \sigma\in\{\pm 1\}}} t_{i,j}^{(\text{round})} \left(a_{i,\sigma}^\dagger a_{j,\sigma} + a_{j,\sigma}^\dagger a_{i,\sigma} \right), \tag{C48}$$

where $c_U^{(\text{main})} = u_\beta^{(\text{Coul})}(0)/4$. The difference $H^{(\text{round})} - H^{(\text{main})} - n \cdot c_T$ contains two types of terms, both of the coefficients of which are $O(\sqrt{\alpha})$: the smaller part of the on-site terms $c_U^{(\text{round})}$ and the off-site terms corresponding to edges in the interaction graph. The following lemma bounds the contribution from this difference.

Lemma 2:

$$\left\| H^{(round)} - H^{(main)} - nc_T \right\| \leq 30n^2\sqrt{\alpha}. \tag{C49}$$

Proof of Lemma 2. First, recall that we are restricting to the fixed-particle-number subspace, in which the diagonal part $c_T \sum_{i,\sigma} n_{i,\sigma}$ of $T^{(\text{round})}$ is the constant $n \cdot c_T$. That is, $T^{(\text{round})} = T^{(\text{main})} + n \cdot c_T$. Let

$$B_2 = B \setminus \{(i,i,i,i) : i \in [n]\} \tag{C50}$$

be the subset of B, the elements of which contain two distinct indices (corresponding to an edge):

$$\left\| H^{(\text{round})} - H^{(\text{main})} - n \cdot c_T \right\| = \left\| U^{(\text{round})} - U^{(\text{main})} \right\| \tag{C51}$$

$$= \left\| \frac{1}{2} \sum_{\substack{(i,j,k,l)\in B \\ \sigma,\tau\in\{\pm 1\}}} u_{i,j,k,l}^{(\text{round})} a_{i,\sigma}^\dagger a_{j,\tau}^\dagger a_{k,\tau} a_{l,\sigma} - c_U^{(\text{main})} \sum_{i\in[n]} n_{i,+1} n_{i,-1} \right\| \tag{C52}$$

$$\leq \sum_{i\in[n]} \left| c_U^{(\text{round})} - c_U^{(\text{main})} \right| + \frac{1}{2} \sum_{\substack{(i,j,k,l)\in B_2 \\ \sigma,\tau\in\{\pm 1\}}} u_{i,j,k,l}^{(\text{round})} \tag{C53}$$

$$= n \frac{1}{4d} u_\alpha^{(\text{Coul})}(0) + \frac{1}{2} \sum_{\substack{(i,j,k,l)\in B_2 \\ \sigma,\tau\in\{\pm 1\}}} u_{i,j,k,l}^{(\text{round})} \tag{C54}$$

$$\leq n \frac{1}{4d} u_\alpha^{(\text{Coul})}(0) + \frac{1}{2} \times \underbrace{4}_{\sigma,\tau} \times \underbrace{14 \times \binom{n}{2}}_{B_2} \times u_\alpha^{(\text{Coul})}(0) \tag{C55}$$

$$\leq 15n^2 u_\alpha^{(\text{Coul})}(0) = 15n^2 \frac{2}{\sqrt{\pi}} \sqrt{\alpha} \leq 30n^2\sqrt{\alpha}. \tag{C56}$$

■

4. Hardness of estimating ground-state energy

Now, we are ready to prove the main theorem.

Proof of Theorem 1. Membership in QMA is straightforward. For hardness, we reduce from the Fermi-Hubbard model. Recall Theorem 2: for some p, q and all $u_0^{(\text{Hubb})} \geq n^{14+3p+2q}$, finding the ground state to precision n^{-q} of

$$H^{(\text{Hubb})} = u_0^{(\text{Hubb})} \sum_{i\in[n]} n_{i,+1} n_{i,-1} + \sum_{i<j} t_{i,j}^{(\text{Hubb})} \left(a_{i,\sigma}^\dagger a_{j,\sigma} + a_{j,\sigma}^\dagger a_{i,\sigma} \right) \tag{C57}$$

subject to $\left|t_{i,j}^{(\mathrm{Hubb})}\right| \leq \sqrt{n^p u_0^{(\mathrm{Hubb})}}$ is QMA-complete. In the preceding sections, we show that, using our choice of single-electron orbitals, the electronic-structure Hamiltonian is close to

$$H^{(\mathrm{ES})} \approx H^{(\mathrm{main})} + n \cdot c_T = c_U^{(\mathrm{main})} n_{i,+1} n_{i,-1} + \sum_{i<j} t_{i,j}^{(\mathrm{round})} \left(a_{i,\sigma}^\dagger a_{j,\sigma} + a_{j,\sigma}^\dagger a_{i,\sigma}\right) + n \cdot c_T. \tag{C58}$$

To prove the theorem, it suffices to show that for any Hubbard Hamiltonian satisfying the conditions of Theorem 2, we can set the parameters $\alpha, \beta, \{\gamma_{i,j}\}_{i,j}, \Gamma$ such that

$$\rho H^{(\mathrm{Hubb})} = H^{(\mathrm{main})} \tag{C59}$$

and

$$\left\| H^{(\mathrm{main})} - H^{(\mathrm{ES})} - n \cdot c_T \right\| = o\left(\rho n^{-q}\right) \tag{C60}$$

for some $\rho \in \mathbb{R}$. With this, finding the ground state of $H^{(\mathrm{ES})}$ to precision $O(\rho n^{-q})$ allows us to find the ground state of $H^{(\mathrm{Hubb})}$ to precision $O(n^{-q})$ and so the former must be QMA hard. We base our parametrization on four constants independent of n:

$$a = \log_n \alpha, \quad b = \log_n \beta, \quad r = \log_n \rho,$$
$$g = -\log_n \sqrt{f(\omega_0)} = -\frac{1}{2}\log_n f(\omega_0), \tag{C61}$$

where ω_0 is a lower bound on $\omega_{i,j}$ to be set later. The first three immediately set α, β, and ρ, respectively. Equating $n^r H^{(\mathrm{Hubb})}$ and $H^{(\mathrm{main})}$ requires

$$n^r u_0^{(\mathrm{Hubb})} = c_U^{(\mathrm{main})} = \frac{1}{2\sqrt{\pi}}\sqrt{\beta}, \tag{C62}$$
$$n^r t_{i,j}^{(\mathrm{Hubb})} = -\frac{\alpha}{4d}\sqrt{f(\omega_{i,j})}. \tag{C63}$$

a. *Coefficient ranges.* If we set

$$\boxed{b = 30 + 6p + 4q + 2r}, \tag{C64}$$

then

$$u_0^{(\mathrm{Hubb})} = \frac{\sqrt{\beta}}{2\sqrt{\pi} n^r} \geq \frac{1}{4}\frac{\sqrt{\beta}}{n^r} = 4^{-1} n^{0.5b-r} = \frac{n}{4} n^{14+3p+2q} \geq n^{14+3p+2q}, \quad n \geq 4 \tag{C65}$$

satisfies the lower bound in the statement of Theorem 2.

If we set

$$\boxed{g = -\frac{1}{2}p + a - \frac{1}{4}b - \frac{3}{2} - \frac{1}{2}r \geq 1}, \tag{C66}$$

then, for $n \geq 9$,

$$\frac{\alpha}{4d}\sqrt{f(\omega_0)} \geq \frac{\alpha}{4n}\sqrt{f(\omega_0)} = \frac{1}{4}n^{a-g-1} = \frac{\sqrt{n}}{4} n^{\frac{1}{2}r+\frac{1}{2}p+\frac{1}{4}b} \tag{C67}$$

$$\geq \frac{3}{4} n^{\frac{1}{2}r+\frac{1}{2}p+\frac{1}{4}b} \tag{C68}$$

$$\geq \frac{1}{\sqrt{2\sqrt{\pi}}} n^{\frac{1}{2}r+\frac{1}{2}p+\frac{1}{4}b} = n^r \sqrt{n^p \frac{n^{-r}\sqrt{\beta}}{2\sqrt{\pi}}} = \rho\sqrt{n^p u_0^{(\mathrm{Hubb})}}, \tag{C69}$$

and thus for any $t_{i,j}^{(\mathrm{Hubb})} \leq \sqrt{n^p u_0^{(\mathrm{Hubb})}}$ there is some $\omega_{i,j} \geq \omega_0$ that satisfies Eq. (C63).

b. *Bounding the difference between electronic structure and Hubbard.* The difference between the electronic-structure Hamiltonian and the main Hamiltonian is

$$\left\| H^{(\mathrm{main})} + n \cdot c_T - H^{(\mathrm{ES})} \right\| \leq \left\| H^{(\mathrm{main})} + n \cdot c_T - H^{(\mathrm{round})} \right\| + \left\| H^{(\mathrm{round})} - H^{(\mathrm{ES})} \right\| \tag{C70}$$

$$\leq 30n^2\sqrt{\alpha} + \frac{1}{20n^2} + 3n^2\alpha f(\omega_{\min}) + 8n^4\sqrt{\alpha}\exp(-\omega_{\min}/2) \tag{C71}$$

$$\leq 30n^2\sqrt{\alpha} + \frac{1}{20n^2} + 3n^2\alpha f(\omega_0) + 8n^4\sqrt{\alpha}\sqrt{f(\omega_0)} \tag{C72}$$

$$= O\left(n^{2+\frac{1}{2}a} + n^{-2} + n^{2+a-2g} + n^{4+\frac{1}{2}a-g}\right) \tag{C73}$$

$$= O\left(n^{4+\frac{1}{2}a} + n^{2+a-2g}\right). \tag{C74}$$

Therefore, to satisfy Eq. (C60), it suffices to have

$$\boxed{4 + \frac{1}{2}a < r - q} \tag{C75}$$

and

$$2 + a - 2g < r - q. \tag{C76}$$

Plugging Eq. (C66) into the latter yields

$$\boxed{p + q + 5 < a - \frac{1}{2}b}. \tag{C77}$$

c. *Parameter setting*. In summary, our constraints are

$$30 + 6p + 4q = b - 2r, \tag{C78}$$

$$\frac{1}{2}p + \frac{5}{2} < a - \frac{1}{4}b - \frac{1}{2}r, \tag{C79}$$

$$4 + q < -\frac{1}{2}a + r, \tag{C80}$$

$$p + q + 5 < a - \frac{1}{2}b. \tag{C81}$$

The following settings satisfy all the required constraints:

$$a = 18p + 12q + 90, \tag{C82}$$

$$b = \frac{5}{3}a, \tag{C83}$$

$$r = \frac{2}{3}a, \tag{C84}$$

$$g = \frac{1}{4}a - \frac{1}{2}p - \frac{3}{2}. \tag{C85}$$

■

APPENDIX D: ADDING IN A POTENTIAL

In this appendix, we describe how Theorem 1 can be strengthened to include a "molecular" external potential; Theorem 3 can also be strengthened in the same way using similar techniques. The basic idea is that, given the orbitals used in the proof of Theorem 1, we can specify a set of nuclear positions such that the contribution to energy is approximately a fixed constant (within the fixed basis of the orbitals). We emphasize that this is only for this specific set of nuclear positions (and charges) and not for arbitrary positions (which would, inter alia, contradict the virial theorem). That being said, this single specification of nuclear positions is sufficient to prove the claim.

Recall that both constructions are based on composite orbitals $(\phi_i)_{i=1}^n$, each a linear combination of primitive Gaussian orbitals $\left(\phi_{i,p}\right)_{p=0}^d$ respectively centered at points $\left(\mathbf{x}_{i,p}\right)_{p=0}^d$ (see Sec. C 1). Suppose we were to add a nucleus with a single proton at each point $\mathbf{x}_{i,p}$, modeled (using the Born-Oppenheimer approximation) as a positive unit point charge. In real space, the single-particle external potential would then be

$$V(\mathbf{r}) = \sum_{i=1}^{n}\sum_{p=0}^{d} V^{(i,p)}(\mathbf{r}) = -\sum_{i=1}^{n}\sum_{p=0}^{d} \left\|\mathbf{r} - \mathbf{x}_{i,p}\right\|^{-1}, \tag{D1}$$

$$V^{(i,p)}(\mathbf{r}) = -\left\|\mathbf{r} - \mathbf{x}_{i,p}\right\|^{-1}, \tag{D2}$$

where $V^{(i,p)}(\mathbf{r})$ is the contribution from the nucleus at $\mathbf{x}_{i,p}$ [below, we use V and $V^{(i,p)}$ refer to the $n(d+1) \times n(d+1)$ matrices the entries of which are the integrals of the above functions in the nonorthonormalized primitive basis, as in Eq. (D5)]:

$$(V)_{(i,p),(j,q)}. \tag{D3}$$

The main goal of this section is to prove the following lemma, where $V^{(\mathrm{ES})}$ is the contribution to the Hamiltonian from these additional interactions (in the orthonormalized basis $\tilde{\boldsymbol{\phi}}$).

Lemma 3: *For* $\alpha \geq 1$, $\omega_{\min} \geq 2$, $\Gamma \geq 2\omega_{\max} + n^9$, *and* $\alpha\Gamma^2 \geq 36\log n + 2\log\beta$,

$$\left\|V^{(ES)} - n \cdot c_V\right\| \leq 37n\sqrt{\alpha}. \tag{D4}$$

Note that Γ is unconstrained from above and so we can always set it large enough to satisfy the conditions of the lemma. More significantly, adding $V^{(\mathrm{ES})}$ as constructed here to $H^{(\mathrm{ES})}$ in the proof of Theorem 1 simply adds $O(n\sqrt{\alpha})$ to Eq. (C70), which is subsumed by the extant $O(n^2\sqrt{\alpha})$ term there, so that the rest of the proof is unaffected. From this, we can conclude the following.

Corollary 1: *Theorem 1 holds even with an external potential induced by positive unit point charges.*

The remainder of this subsection lays out the ingredients of the proof of Lemma 3 and concludes with the formal proof putting them together.

As in Sec. C 2, we define the pair of $n(d+1) \times n(d+1)$ matrices $V^{(i,p)}$ and $\tilde{V}^{(i,p)}$ with entries

$$v^{(i',p')}_{(i,p),(j,q)} = \left(V^{(i',p')}\right)_{(i,p),(j,q)} = \int d\mathbf{r}\phi^*_{i,p}(\mathbf{r})V^{(i',p')}(\mathbf{r})\phi_{j,q}(\mathbf{r}), \tag{D5}$$

$$\tilde{v}^{(i',p')}_{(i,p),(j,q)} = \left(\tilde{V}^{(i',p')}\right)_{(i,p),(j,q)} = \int d\mathbf{r}\tilde{\phi}^*_{i,p}(\mathbf{r})V^{(i',p')}(\mathbf{r})\tilde{\phi}_{j,q}(\mathbf{r}). \tag{D6}$$

They are related by

$$\tilde{V}^{(i,p)} = S^{-1/2}V^{(i,p)}S^{-1/2} = RV^{(i,p)}R, \tag{D7}$$

where S is the overlap matrix of the primitive orbitals $\left(\phi_{i,p}\right)_{i,p}$ and $R = S^{-1/2}$. In the composite orthonormalized basis $\left(\tilde{\phi}_i\right)_i$, we have the potential operator

$$V^{(\mathrm{ES})} = \sum_{\substack{i,j\in[n]\\ \sigma\in\{\pm1\}}} \tilde{v}_{i,j}\tilde{a}^\dagger_{i,\sigma}\tilde{a}_{j,\sigma}, \tag{D8}$$

where

$$\tilde{v}_{i,j} = \sum_{i',p'} \tilde{v}^{(i',p')}_{i,j}, \tag{D9}$$

$$\tilde{v}_{i,j}^{(i',p')} = \int d\mathbf{r}\tilde{\phi}_i^*(\mathbf{r})V^{(i',p')}\tilde{\phi}_j(\mathbf{r}) = \sum_{p,q}\psi_p\psi_q\tilde{v}_{(i,p),(j,q)}^{(i',p')}. \tag{D10}$$

We define the utility function

$$v_{\mu,\nu}(\mathbf{y},\mathbf{x}) = \int d\mathbf{r}\xi_\mu(\mathbf{r})\xi_\nu(\mathbf{r}-\mathbf{x})\|\mathbf{r}-\mathbf{y}\|^{-1} \tag{D11}$$

corresponding to the magnitude of two Gaussians (with exponents μ and ν and with centers $\mathbf{0}$ and $\mathbf{x}$, respectively) interacting with a unit point charge at $\mathbf{y}$. Note that when both $\mathbf{x}$ and $\mathbf{y}$ are nonzero, this definition is not symmetric with respect to the two Gaussians and depends on the relative positions of $\mathbf{x}$ and $\mathbf{y}$. However, when $\mathbf{y}=\mathbf{0}$, v depends only on the magnitude $\|\mathbf{x}\|$ of $\mathbf{x}$. Furthermore, when $\mathbf{x}=\mathbf{0}$ (i.e., the two Gaussians have identical centers), then v is symmetric with respect to the two Gaussians and depends only on the magnitude $\|\mathbf{y}\|$ of $\mathbf{y}$. The following summarizes some useful facts.

Fact 1: *For $\mu \geq \nu > 0$,*

$$v_{\mu,\nu}(\mathbf{y},\mathbf{x}) = \exp\left(-\frac{\mu\nu}{\mu+\nu}\|\mathbf{x}\|^2\right) v_{\frac{\mu+\nu}{2},\frac{\mu+\nu}{2}}\left(\mathbf{y}-\frac{\nu}{\mu+\nu}\mathbf{x},\mathbf{0}\right) \tag{D12}$$

$$= 2\sqrt{\frac{\mu+\nu}{\pi}}\exp\left(-\frac{\mu\nu}{\mu+\nu}\|\mathbf{x}\|^2\right) F_0\left((\mu+\nu)\left\|\mathbf{y}-\frac{\nu}{\mu+\nu}\mathbf{x}\right\|^2\right) \tag{D13}$$

$$\leq 2\sqrt{\frac{2\mu}{\pi}}\exp\left(-\frac{\nu}{2}\|\mathbf{x}\|^2\right) F_0\left(2\nu\left\|\mathbf{y}-\frac{\nu}{\mu+\nu}\mathbf{x}\right\|^2\right) \tag{D14}$$

$$\leq 2\sqrt{\frac{2\mu}{\pi}}\exp\left(-\frac{\nu}{2}\|\mathbf{x}\|^2\right), \tag{D15}$$

$$v_{\mu,\mu}(\mathbf{0},\mathbf{0}) = 2\sqrt{2\mu/\pi}, \tag{D16}$$

$$v_{\mu,\mu}(\mathbf{x},\mathbf{0}) = v_{\mu,\mu}(\mathbf{0},\mathbf{0})F_0(2\mu\|\mathbf{x}\|^2), \tag{D17}$$

$$v_{\mu,\mu}(\mathbf{0},\mathbf{x}) = \exp(-\mu\|\mathbf{x}\|^2/2)v_{\mu,\mu}(\mathbf{x}/2,\mathbf{0}). \tag{D18}$$

Consider the element $v_{(i,p),(j,q)}^{(i',p')}$, the integral of two Gaussians centered at $\mathbf{x}_{i,p}$ and $\mathbf{x}_{j,q}$ interacting with a nucleus at $\mathbf{x}_{i',p'}$. For most triples $(i,p),(j,q),(i',p')$, at least one of these points is at least Γ away from the others. There are two exceptions. The first is when all three points are the same and in a singleton block: $i=j=i'$ and $p=q=p' \notin \{1,\ldots,\deg_i\}$. This corresponds to this situation in which the nuclear charge and the two primitive orbitals are centered at the same point $\mathbf{x}_{i,p}$ which is at least a distance Γ from all other points. The second case corresponds to the situation in which the three points are all contained in $\mathcal{B}(i,j)$ for some edge $\{i,j\}$ in the original graph. The set $\mathcal{B}(i,j)$ contains the two indices for the points that are $\gamma_{i,j}$ apart from each other in the construction. We define the matrix $V^{(\text{block})}$ to include only contributions arising from such exceptions. That is, we define the elements of $V^{(\text{block})}$ in the following way. For fixed i and $p \in \{0,\deg_i+1,\ldots,d\}$,

$$v_{(i,p),(i,p)}^{(\text{block})} = v_{(i,p),(i,p)}^{(i,p)}. \tag{D19}$$

For adjacent vertices i and j, where $\mathcal{B}(i,j)=\{(i,p),(j,q)\}$, the block $V_{i,j}^{(\text{block})}$ is the 2×2 submatrix the elements of which are in a row and column from $\mathcal{B}(i,j)$. The on-diagonal entries of $V_{i,j}^{(\text{block})}$ are

$$v_{(i,p),(i,p)}^{(\text{block})} = v_{(i,p),(i,p)}^{(i,p)} + v_{(i,p),(i,p)}^{(j,q)}. \tag{D20}$$

The off-diagonal entries of $V_{i,j}^{(\text{block})}$ are

$$v_{(i,p),(j,q)}^{(\text{block})} = v_{(i,p),(j,q)}^{(i,p)} + v_{(i,p),(j,q)}^{(j,q)}. \tag{D21}$$

Since the block $V_{i,j}^{(\text{block})}$ is symmetric and has the same on-diagonal entries, we can define ON and OFF as:

$$\text{ON}\left(V_{i,j}^{(\text{block})}\right) = v_{(i,p),(i,p)}^{(i,p)} + v_{(i,p),(i,p)}^{(j,q)} \tag{D22}$$

$$= v_{\alpha,\alpha}(0,0) + v_{\alpha,\alpha}(\gamma_{i,j},0) \tag{D23}$$

$$= v_{\alpha,\alpha}(0,0)\left[1+F_0(2\alpha\gamma_{i,j}^2)\right]$$

$$= 2\sqrt{2\alpha/\pi}\left[1+F_0(2\omega_{i,j})\right], \tag{D24}$$

$$\mathrm{OFF}\left(V_{i,j}^{(\mathrm{block})}\right) = v_{(i,p),(j,q)}^{(i,p)} + v_{(i,p),(j,q)}^{(j,q)} \tag{D25}$$

$$= v_{\alpha,\alpha}(0,\gamma_{i,j}) + v_{\alpha,\alpha}(\gamma_{i,j},\gamma_{i,j})$$

$$= 2v_{\alpha,\alpha}(0,\gamma_{i,j}) \tag{D26}$$

$$= 2v_{\alpha,\alpha}(0,0)\exp(-\alpha\gamma_{i,j}^2/2)F_0(\alpha\gamma_{i,j}/2)$$

$$= 4\sqrt{2\alpha/\pi}\epsilon_{i,j}F_0(\omega_{i,j}/2). \tag{D27}$$

We now define an approximate potential operator

$$V^{(\mathrm{aprx})} = \sum_{\substack{i,j\in[n]\\ \sigma\in\{\pm1\}}} \tilde{v}_{i,j}^{(\mathrm{aprx})}\tilde{a}_{i,\sigma}^\dagger\tilde{a}_{j,\sigma},\approx V^{(\mathrm{ES})}, \tag{D28}$$

$$\tilde{v}_{i,j}^{(\mathrm{aprx})} = \sum_{p,q}\psi_p\psi_q\tilde{v}_{(i,p),(j,q)}^{(\mathrm{aprx})}, \tag{D29}$$

$$\tilde{V}^{(\mathrm{aprx})} = R^{(\mathrm{aprx})}\cdot V^{(\mathrm{block})}\cdot R^{(\mathrm{aprx})}, \tag{D30}$$

where $R^{(\mathrm{aprx})}$ is the block-diagonal approximation of R defined in Appendix E.

The following lemma, proved in Sec. D 3, bounds the error introduced by this approximation.

Lemma 4: *For* $\Gamma \geq 2\omega_{\max} + n^9$ *and* $\alpha\Gamma^2 \geq 36\log n + 2\log\beta$,

$$\left\| V^{(ES)} - V^{(aprx)} \right\| \leq 32n. \tag{D31}$$

The following lemma, proved in Sec. D 1, shows that the approximate potential operator is not too big.

Lemma 5: *For* $\omega_{\min} \geq 2$,

$$\left\| V^{(aprx)} - n\cdot c_V \right\| \leq 5n\sqrt{\alpha}. \tag{D32}$$

Putting these together, we can prove Lemma 3.

Proof of Lemma 3. Under the conditions of the lemma, Lemmas 4 and 5 imply

$$\left\| V^{(\mathrm{ES})} - n\cdot c_V \right\| \leq \left\| V^{(\mathrm{ES})} - V^{(\mathrm{aprx})} \right\| + \left\| V^{(\mathrm{aprx})} - n\cdot c_V \right\| \tag{D33}$$

$$\leq 32n + 5n\sqrt{\alpha} \leq 37n\sqrt{\alpha}. \tag{D34}$$

■

1. Proof of Lemma 5

Let j be the pth neighbor of i and i the qth neighbor of j. Then the elements of $\tilde{V}^{(\mathrm{aprx})}$ are

$$\tilde{v}_{(i,p),(i,p)}^{(\mathrm{aprx})} = \mathrm{ON}(R_{i,j}\cdot V_{i,j}^{(\mathrm{block})}\cdot R_{i,j}) \tag{D35}$$

$$= \frac{v_{(i,p),(i,p)}^{(\mathrm{block})} - \epsilon_{i,j}v_{(i,p),(j,q)}^{(\mathrm{block})}}{1-\epsilon_{i,j}^2} \tag{D36}$$

$$= v_{\alpha,\alpha}(0,0)\frac{[1+F_0(2\omega_{i,j})] - 2\epsilon_{i,j}^2F_0(\omega_{i,j}/2)}{1-\epsilon_{i,j}^2} \tag{D37}$$

$$= v_{\alpha,\alpha}(0,0)\left\{1 + \frac{F_0(2\omega_{i,j}) + \epsilon_{i,j}^2[1-2F_0(\omega_{i,j}/2)]}{1-\epsilon_{i,j}^2}\right\}, \tag{D38}$$

$$\tilde{v}_{(i,p),(j,q)}^{(\mathrm{aprx})} = \mathrm{OFF}(R_{i,j}\cdot V_{i,j}^{(\mathrm{block})}\cdot R_{i,j}) \tag{D39}$$

$$= \frac{v_{(i,p),(j,q)}^{(\mathrm{block})} - \epsilon_{i,j}v_{(i,p),(i,p)}^{(\mathrm{block})}}{1-\epsilon_{i,j}^2} \tag{D40}$$

$$= v_{\alpha,\alpha}(0,0)\frac{\epsilon_{i,j}}{1-\epsilon_{i,j}^2}\left\{2F_0(\omega_{i,j}/2) - [1+F_0(2\omega_{i,j})]\right\}. \tag{D41}$$

Note that for $p = 0$ or $p > \deg_i$, $\tilde{v}_{(i,p),(i,p)}^{(\mathrm{aprx})} = v_{(i,p),(i,p)}^{(\mathrm{block})}$.

In the composite basis, the diagonal coefficients are

$$\tilde{v}^{(\mathrm{aprx})}_{i,i} = \sum_{p',q'} \psi_p \psi_q \tilde{v}^{(\mathrm{aprx})}_{(i,p'),(j,q')} = \frac{1}{2d} \sum_{p} \tilde{v}^{(\mathrm{aprx})}_{(i,p),(i,p)} \tag{D42}$$

$$= c_V + \frac{v_{\alpha,\alpha}(0,0)}{2d} \sum_{j:\{i,j\}\in E} \frac{F_0(2\omega_{i,j}) + \epsilon^2_{i,j}[1 - 2F_0(\omega_{i,j}/2)]}{1-\epsilon^2_{i,j}}. \tag{D43}$$

Later, we use the fact that

$$\left| \frac{F_0(2\omega_{i,j}) + \epsilon^2_{i,j}[1 - 2F_0(\omega_{i,j}/2)]}{1-\epsilon^2_{i,j}} \right| \leq \frac{\left|F_0(2\omega_{i,j})\right| + \epsilon^2_{i,j}\left|1 - 2F_0(\omega_{i,j}/2)\right|}{1-\epsilon^2_{i,j}} \tag{D44}$$

$$\leq \frac{1+\epsilon^2_{i,j}}{1-\epsilon^2_{i,j}} \leq 2. \tag{D45}$$

The off-diagonal coefficients in the composite basis are

$$\tilde{v}^{(\mathrm{aprx})}_{i,j} = \sum_{p',q'} \psi_{p'} \psi_{q'} \tilde{v}^{(\mathrm{aprx})}_{(i,p'),(i,q')} = \frac{1}{2d} \tilde{v}^{(\mathrm{aprx})}_{(i,p),(j,q)} \tag{D46}$$

$$= \frac{v_{\alpha,\alpha}(0,0)}{2d} \frac{\epsilon_{i,j}}{1-\epsilon^2_{i,j}} \left[2F_0(\omega_{i,j}/2) - (1 + F_0(2\omega_{i,j}))\right] \tag{D47}$$

$$\left|\tilde{v}^{(\mathrm{aprx})}_{i,j}\right| \leq \frac{\epsilon_{i,j}}{1-\epsilon^2_{i,j}} \leq 1. \tag{D48}$$

Putting it all together,

$$\left\| V^{(\mathrm{aprx})} - n \cdot c_V \right\| \tag{D49}$$

$$= \left\| \sum_{\substack{i,j \\ \sigma}} \tilde{v}^{(\mathrm{aprx})}_{i,j} \tilde{a}^\dagger_{i,\sigma} \tilde{a}_{j,\sigma} - n \cdot c_V \right\| \tag{D50}$$

$$\leq \left\| \sum_{\substack{i \\ \sigma}} c_V \tilde{n}_{i,\sigma} - n \cdot c_V \right\| + \frac{v_{\alpha,\alpha}(0,0)}{2d} \left\| \sum_{\substack{i \\ \sigma}} \sum_{j:\{i,j\}\in E} \frac{F_0(2\omega_{i,j}) + \epsilon^2_{i,j}[1 - 2F_0(\omega_{i,j}/2)]}{1-\epsilon^2_{i,j}} \tilde{n}_{i,\sigma} \right\| \tag{D51}$$

$$+ \frac{v_{\alpha,\alpha}}{2d} \left\| \sum_{\substack{\{i,j\}\in E \\ \sigma}} \frac{\epsilon_{i,j}}{1-\epsilon^2_{i,j}} \left\{2F_0(\omega_{i,j}/2) - [1 + F_0(2\omega_{i,j})]\right\} \left(\tilde{a}^\dagger_{i,\sigma} \tilde{a}_{j,\sigma} + \mathrm{h.c.}\right) \right\| \tag{D52}$$

$$\leq \frac{2 v_{\alpha,\alpha}(0,0)}{d} \sum_{\{i,j\}\in E} [1+2] \tag{D53}$$

$$\leq \frac{2}{d} 2\sqrt{2\alpha/\pi} \frac{nd}{2} 3 \leq 5n\sqrt{\alpha}. \tag{D54}$$

■

2. Proof of Fact 1

$$v_{\alpha,\beta}(\mathbf{y},\mathbf{x}) = \left(\frac{2\alpha}{\pi}\right)^{3/2} \int d\mathbf{r} \exp\left(-\alpha\|\mathbf{r}\|^2 - \|\mathbf{r}-\mathbf{x}\|^2\right) \|\mathbf{r}-\mathbf{y}\|^{-1} \tag{D55}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2} \exp\left(-\frac{\alpha\beta}{\alpha+\beta}\|\mathbf{x}\|^2\right) \int d\mathbf{r} \exp\left[-(\alpha+\beta)\left\|\mathbf{r}-\frac{\beta}{\alpha+\beta}\mathbf{x}\right\|^2\right] \|\mathbf{r}-\mathbf{y}\|^{-1} \tag{D56}$$

$$= \exp\left(-\frac{\alpha\beta}{\alpha+\beta}\|\mathbf{x}\|^2\right) \left\{\left(\frac{2\alpha}{\pi}\right)^{3/2} \int d\mathbf{r} \exp\left[-(\alpha+\beta)\|\mathbf{r}\|^2\right] \left\|\mathbf{r}-\left(\mathbf{y}-\frac{\beta}{\alpha+\beta}\mathbf{x}\right)\right\|^{-1}\right\} \tag{D57}$$

$$= \exp\left(-\frac{\alpha\beta}{\alpha+\beta}\|\mathbf{x}\|^2\right) v_{\frac{\alpha+\beta}{2},\frac{\alpha+\beta}{2}}\left(\mathbf{y}-\frac{\beta}{\alpha+\beta}\mathbf{x},\mathbf{0}\right), \tag{D58}$$

$$v_{\alpha,\alpha}(\mathbf{0},\mathbf{0}) = \int d\mathbf{r}\xi_\alpha(\mathbf{r})^2\|\mathbf{r}\|^{-1} \tag{D59}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2} \int d\mathbf{r} \exp(-2\alpha\|\mathbf{r}\|^2)\|\mathbf{r}\|^{-1} \tag{D60}$$

$$= \frac{2^{7/2}\alpha^{3/2}}{\pi^{1/2}} \int_0^\infty dr \exp(-2\alpha r^2) r \tag{D61}$$

$$= -\frac{2^{3/2}\alpha^{1/2}}{\pi^{1/2}} e^{-2\alpha r^2}\Big|_{r=0}^{\infty} \tag{D62}$$

$$= \frac{2^{3/2}\alpha^{1/2}}{\pi^{1/2}}, \tag{D63}$$

$$v_{\alpha,\alpha}(\mathbf{x},\mathbf{0}) = \int d\mathbf{r}\xi_\alpha(\mathbf{r})^2\|\mathbf{r}-\mathbf{x}\|^{-1} \tag{D64}$$

$$= 2\left(\frac{2\alpha}{\pi}\right)^{1/2} F_0(2\alpha\|\mathbf{x}\|^2), \tag{D65}$$

$$v_{\alpha,\alpha}(\mathbf{0},\mathbf{x}) = \int d\mathbf{r}\xi_\alpha(\mathbf{r}-x\mathbf{e}_1)\xi_\alpha(\mathbf{r})\|\mathbf{r}\|^{-1} \tag{D66}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2} \int d\mathbf{r} \exp\left[-\alpha\left(\|\mathbf{r}\|^2 + \|\mathbf{r}-\mathbf{x}\|^2\right)\right] \|\mathbf{r}\|^{-1} \tag{D67}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/2} \exp(-\alpha\|\mathbf{x}\|^2/2) \int d\mathbf{r} \exp\left[-2\alpha\left(\left\|\mathbf{r}-\frac{\mathbf{x}}{2}\right\|^2\right)\right] \|\mathbf{r}\|^{-1} \tag{D68}$$

$$= \exp(-\alpha\|\mathbf{x}\|^2/2) \left\{\left(\frac{2\alpha}{\pi}\right)^{3/2} \int d\mathbf{r} \exp\left[-2\alpha\left(\|\mathbf{r}\|^2\right)\right] \|\mathbf{r}+\frac{\mathbf{x}}{2}\|^{-1}\right\} \tag{D69}$$

$$= \exp(-\alpha\|\mathbf{x}\|^2/2) v_\alpha(\mathbf{x}/2,\mathbf{0}). \tag{D70}$$

■

3. Proof of Lemma 4

Lemma 6: *For* $\Gamma \geq 2\gamma_{\max}$,

$$v_{\max} \leq 2n^2\sqrt{\beta} \tag{D71}$$

$$v_{\max}^{(neg)} \leq 2n^2 \max\left\{\sqrt{\beta}\exp(-\alpha\Gamma^2/2), 1/\Gamma\right\}. \tag{D72}$$

The proof is deferred to the end of this subsection.
Using the same logic as in Eq. (E23) *et seq*.,

$$\max\left|\tilde{V}-\tilde{V}^{(\mathrm{aprx})}\right| \le n^4\left[(r_{\max})^2 v_{\max}^{(\mathrm{neg})} + 4v_{\max}r_{\max}^{(\mathrm{neg})}\right] \tag{D73}$$

$$\le n^4\left[4\times 2n^2\max\left\{\sqrt{\beta}\exp(-\alpha\Gamma^2/2), 1/\Gamma\right\} + 4\times 2n^2\sqrt{\beta}n^2\exp[-(\alpha\Gamma^2-\omega_{\min})/2]\right] \tag{D74}$$

$$= 8n^6\left[\max\left\{\sqrt{\beta}\exp(-\alpha\Gamma^2/2), 1/\Gamma\right\} + \sqrt{\beta}n^2\exp[-(\alpha\Gamma^2-\omega_{\min})/2]\right] \tag{D75}$$

$$\le 8n^6\left[\max\left\{\sqrt{\beta}\exp(-\alpha\Gamma^2/2), 1/\Gamma\right\} + \sqrt{\beta}n^2\exp(-\alpha\Gamma^2/4)\right] \tag{D76}$$

$$\le 16n^8\max\left\{\sqrt{\beta}\exp(-\alpha\Gamma^2/4), 1/\Gamma\right\} \tag{D77}$$

$$\le 16n^8\max\left\{\sqrt{\beta}\exp[-(36\log n + 2\log\beta)/4], n^{-9}\right\} \le 16n^{-1}, \tag{D78}$$

where we use the fact that $\Gamma \ge 2\gamma_{\max}$ (a condition of the lemma) implies $\alpha\Gamma^2 \ge 2\omega_{\min}$, as well as the conditions of the lemma directly in the last few lines. Therefore,

$$\left\|V^{(\mathrm{ES})} - V^{(\mathrm{aprx})}\right| = \left\|\sum_{\substack{i,j\\ \sigma}}\left(\tilde{v}_{i,j} - \tilde{v}_{i,j}^{(\mathrm{aprx})}\right)\tilde{a}_{i,\sigma}^{\dagger}a_{j,\sigma}\right| \tag{D79}$$

$$\le 2\sum_{i,j}\left|\tilde{v}_{i,j} - \tilde{v}_{i,j}^{(\mathrm{aprx})}\right| \tag{D80}$$

$$\le 2n^2\times 16n^{-1} \le 32n. \tag{D81}$$

Proof of Lemma 6. We start with $v_{\max}$:

$$v_{\max} = \max|V| = \max_{(i,p),(j,q)}\left|v_{(i,j),(p,q)}\right| \tag{D82}$$

$$\le \max_{(i,p),(j,q)}\sum_{(i',p')}\left|v_{(i,p),(j,q)}^{(i',p')}\right| \tag{D83}$$

$$\le n^2\max_{(i,p),(j,q),(i',p')}\left|v_{(i,p),(j,q)}^{(i',p')}\right| \tag{D84}$$

$$= n^2\max_{i,j,(i',p')}\left\{\left|v_{(i,0),(p,q)}^{(i',p')}\right|, \max_{q>0}\left|v_{(i,0),(j,q)}^{(i',p')}\right|, \max_{p>0,q>0}\left|v_{(i,p),(j,q)}^{(i',p')}\right|\right\} \tag{D85}$$

$$= n^2\max_{i,j,(i',p')}\left\{v_{\beta,\beta}\left(\mathbf{x}_{i',p'}-\mathbf{x}_{i,0},\mathbf{x}_{j,0}-\mathbf{x}_{i,0}\right), \max_{q>0}v_{\beta,\alpha}\left(\mathbf{x}_{i',p'}-\mathbf{x}_{i,0},\mathbf{x}_{j,q}-\mathbf{x}_{i,0}\right)\right.$$
$$\left.\max_{p>0,q>0}v_{\alpha,\alpha}\left(\mathbf{x}_{i',p'}-\mathbf{x}_{i,0},\mathbf{x}_{j,q}-\mathbf{x}_{i,p}\right)\right\} \tag{D86}$$

$$\le \frac{2^{3/2}}{\pi^{1/2}}n^2\sqrt{\beta} \le 2n^2\sqrt{\beta}, \tag{D87}$$

where we use the fact that

$$v_{\mu,\nu}(\mathbf{y},\mathbf{x}) = \exp\left(-\frac{\mu\nu}{\mu+\nu}\|\mathbf{x}\|^2\right)v_{\frac{\mu+\nu}{2},\frac{\mu+\nu}{2}}\left(\mathbf{y}-\frac{\nu}{\mu+\nu}\right) \le v_{\frac{\mu+\nu}{2},\frac{\mu+\nu}{2}}\left(\mathbf{y}-\frac{\nu}{\mu+\nu}\right) \tag{D88}$$

$$= v_{\frac{\mu+\nu}{2},\frac{\mu+\nu}{2}}(\mathbf{0},\mathbf{0})F_0\left[(\mu+\nu)\left\|\mathbf{y}-\frac{\nu}{\mu+\nu}\right\|^2\right] \le v_{\frac{\mu+\nu}{2},\frac{\mu+\nu}{2}}(\mathbf{0},\mathbf{0}) = 2\sqrt{(\mu+\nu)/\pi}. \tag{D89}$$

Now we turn our attention to $v_{\max}^{(\mathrm{neg})} = \max_{(i,p),(j,q)} \left| v_{(i,p),(j,q)}^{(\mathrm{neg})} \right\|$. Recall that $V^{(\mathrm{neg})} = V - V^{(\mathrm{block})}$, where $V^{(\mathrm{block})}$ includes only contributions from Gaussians and nuclei that are mutually "close" ($\ll \Gamma$) to each other.

Let us consider the maximand in three cases.

a. *Case 1*. (i,p) and (j,q) are in different blocks. Let

$$v_{(i,p),(j,q)}^{(\mathrm{neg})} = \sum_{(i',p')} v_{(i,0),(i,0)}^{(\mathrm{neg}(i',p'))} \tag{D90}$$

$$\leq \sum_{(i',p')} 2\sqrt{2\beta/\pi}\, \exp(-\alpha\Gamma^2/2) \tag{D91}$$

$$\leq 2n^2\sqrt{2\beta/\pi}\, \exp(-\alpha\Gamma^2/2) \leq 2n^2\sqrt{\beta}\, \exp(-\alpha\Gamma^2/2). \tag{D92}$$

b. *Case 2* $i = j$ and $p = q = 0$. In this case,

$$v_{(i,0),(j,0)}^{(\mathrm{neg})} = \sum_{(i',p')\neq(i,0)} v_{(i,0),(j,0)}^{(\mathrm{neg}(i',p'))} \tag{D93}$$

$$= \sum_{(i',p')\neq(i,0)} v_{\beta,\beta}(\mathbf{x}_{i',p'} - \mathbf{x}_{i,0}, \mathbf{0}) \tag{D94}$$

$$\leq n^2 2\sqrt{2\beta/\pi} F_0(2\beta\Gamma^2) \tag{D95}$$

$$\leq n^2 2\sqrt{2\beta/\pi}\frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{2\beta\Gamma^2}} = n^2/\Gamma. \tag{D96}$$

c. *Case 3*. (i,p) and (j,q) are in the same block and $p \neq 0$. (This implies that $q > 0$.) Let j' be the pth neighbor of i and i the q'th neighbor of j'. This case includes both $(j,q) = (i,p)$ and $(j,q) = (j',q')$:

$$v_{(i,p),(j,q)}^{(\mathrm{neg})} = \sum_{(i',p')\neq(i,p),(j,q)} v_{(i,p),(j,q)}^{(\mathrm{neg}(i',p'))} \tag{D97}$$

$$= \sum_{(i',p')\notin\{(i,p),(j',q')\}} v_{\alpha,\alpha}(\mathbf{x}_{i',p'} - \mathbf{x}_{i,p}, \mathbf{x}_{j,q} - \mathbf{x}_{i,p}) \tag{D98}$$

$$= 2\sqrt{2\alpha/\pi} \sum_{(i',p')\notin\{(i,p),(j',q')\}} \exp\left(-\alpha\left\|\mathbf{x}_{j,q} - \mathbf{x}_{i,p}\right\|^2/2\right) F_0\left[2\alpha\left\|\mathbf{x}_{i',p'} - \mathbf{x}_{i,p} - \frac{1}{2}\left(\mathbf{x}_{j,q} - \mathbf{x}_{i,p}\right)\right\|^2\right] \tag{D99}$$

$$\leq 2\sqrt{2\alpha/\pi} \sum_{(i',p')\notin\{(i,p),(j',q')\}} F_0\left[2\alpha\left\|\mathbf{x}_{i',p'} - \frac{1}{2}\left(\mathbf{x}_{j,q} + \mathbf{x}_{i,p}\right)\right\|^2\right] \tag{D100}$$

$$\leq \sum_{(i',p')\notin\{(i,p),(j',q')\}} 2\sqrt{2\alpha/\pi} F_0\left[2\alpha\left(\Gamma - \gamma_{i,j}\right)^2\right] \tag{D101}$$

$$\leq n^2 2\sqrt{2\alpha/\pi} F_0\left(\alpha\Gamma^2/2\right) \tag{D102}$$

$$\leq n^2 2\sqrt{2\alpha/\pi}\frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{\alpha\Gamma^2/2}} = \frac{2n^2}{\Gamma}. \tag{D103}$$

■

APPENDIX E: PROOF OF LEMMA 1

The proof of Lemma 1 uses the following technical lemmas that quantify the statement that matrices $\tilde{T}$, S, and $\tilde{U}$ are approximately block diagonal. It is convenient to refer only to the entries along the diagonal or inside the edge blocks. For an $n(d+1) \times n(d+1)$ matrix or an $n^2(d+1)^2 \times n^2(d+1)^2$ matrix A, let $A^{(\text{block})}$ denote the matrix obtained by replacing all of the off-diagonal entries of A outside the edge blocks with 0. Define

$$S^{(\text{neg})} = S - S^{(\text{block})}, \tag{E1}$$

$$R = S^{-1/2}, \tag{E2}$$

$$R^{(\text{aprx})} = \left(S^{(\text{block})}\right)^{-1/2}, \tag{E3}$$

$$R^{(\text{neg})} = R - R^{(\text{aprx})}. \tag{E4}$$

Note that, because $S^{(\text{block})}$ is block diagonal, $R^{(\text{aprx})}$ is also block diagonal. However, $R^{(\text{block})} \neq R^{(\text{aprx})}$. The matrix $R^{(\text{neg})}$, unlike $S^{(\text{neg})}$, has nonzero entries even on the diagonal and within the blocks, though these are small.

The first lemma bounds $\max(|R^{(\text{neg})}|)$, where $\max(|A|)$ is defined to be the maximum of the absolute values of the entries in matrix A.

Lemma 7: *If* $\alpha\Gamma^2 \geq 4\log n + 2\omega_{\min} + 2$ *and* $\omega_{\min} \geq 4$, *then*

$$r^{(neg)}_{\max} = \max\left(\left|R^{(neg)}\right|\right) \leq n^2 \exp\left[-(\alpha\Gamma^2 - \omega_{\min})/2\right]. \tag{E5}$$

Corollary 2: *For* $\alpha\Gamma^2 \geq 4\log n + 2\omega_{\min} + 2$ *and* $\omega_{\min} \geq 2$,

$$\begin{aligned} r^{(neg)}_{\max} &\leq n^2 \exp\left[-\left(\alpha\Gamma^2 - \omega_{\min}\right)/2\right] \\ &\leq n^2 \exp\left[-\left(4\log n + 2\omega_{\min} + 2 - \omega_{\min}\right)/2\right] \\ &\leq \exp(-1) \leq 1/2. \end{aligned} \tag{E6}$$

The entries of matrix S are just the overlap of normalized Gaussians, so the diagonal is all ones. Block $S_{i,j}$ corresponding to edge $\{i,j\}$, where $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$ is

$$S_{i,j} = \begin{pmatrix} 1 & \epsilon_{i,j} \\ \epsilon_{i,j} & 1 \end{pmatrix}, \tag{E7}$$

$$\epsilon_{i,j} = s_{(i,p),(j,q)} = s_\alpha(\gamma_{i,j}) = \exp(-\omega_{i,j}/2), \quad \text{where } \omega_{i,j} = \alpha\gamma^2_{i,j}. \tag{E8}$$

The entry $s_{(i,p),(i,p)}$ is not contained in an edge block if and only if $p = 0$ or $p > \deg_i$. In this case, the orbital $\phi_{i,p}$ is at least a distance Γ away from every other primitive orbital and the block for $s_{(i,p),(i,p)}$ is just the single element on the diagonal. For these primitive orbitals, we have

$$s_{(i,p),(i,p)} = r^{(\text{aprx})}_{(i,p),(i,p)} = 1.$$

The edge blocks of $R^{(\text{aprx})}$ can be computed exactly as

$$R^{(\text{aprx})}_{i,j} = \left(S_{i,j}\right)^{-1/2} \tag{E9}$$

$$= \frac{1}{2}\begin{pmatrix} \frac{1}{\sqrt{1+\epsilon_{i,j}}} + \frac{1}{\sqrt{1-\epsilon_{i,j}}} & \frac{1}{\sqrt{1+\epsilon_{i,j}}} - \frac{1}{\sqrt{1-\epsilon_{i,j}}} \\ \frac{1}{\sqrt{1+\epsilon_{i,j}}} - \frac{1}{\sqrt{1-\epsilon_{i,j}}} & \frac{1}{\sqrt{1+\epsilon_{i,j}}} + \frac{1}{\sqrt{1-\epsilon_{i,j}}} \end{pmatrix}. \tag{E10}$$

The following lemma bounds the error from just taking the leading term in $\epsilon_{i,j}$. Note that the 2×2 matrix $R^{(\text{aprx})}_{i,j}$ has identical on-diagonal entries and identical off-diagonal entries. Let $\text{ON}(R^{(\text{aprx})}_{i,j})$ refer to the value of the on-diagonal entries and let $\text{OFF}(R^{(\text{aprx})}_{i,j})$ refer to the value of the off-diagonal entries. The matrix $R^{(\text{aprx})}_{i,j} T_{i,j} R^{(\text{aprx})}_{i,j}$ has the same symmetries, so we can define ON and OFF for those matrices as well.

Lemma 8: *For* $\omega_{\min} \geq 4$ *and* $\{i,j\} \in E$ *where* $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$,

$$1 \leq \text{ON}(r^{(aprx)}) \leq 1 + \epsilon^2_{i,j}, \tag{E11}$$

$$-\frac{\epsilon_{i,j}}{2} - \epsilon^3_{i,j} \leq \text{OFF}(r^{(aprx)}) \leq -\frac{\epsilon_{i,j}}{2}, \tag{E12}$$

$$t_\alpha(0) \leq \text{ON}\left(R^{(aprx)}_{i,j} T_{i,j} R^{(aprx)}_{i,j}\right) \leq t_\alpha(0) + \alpha\omega_{i,j}\epsilon^2_{i,j}, \tag{E13}$$

$$-\frac{\alpha}{2}\sqrt{f(\omega_{i,j})}(1 + 4\epsilon^2_{i,j}) \leq \text{OFF}\left(R^{(aprx)}_{i,j} T_{i,j} R^{(aprx)}_{i,j}\right) \leq -\frac{\alpha}{2}\sqrt{f(\omega_{i,j})}, \tag{E14}$$

$$\max\left[\left|\left(R^{(aprx)}_{i,j}\right)^{\otimes 2} U_{i,j} \left(R^{(aprx)}_{i,j}\right)^{\otimes 2} - U_{i,j}\right|\right] \leq 16\sqrt{\alpha}\epsilon_{i,j}. \tag{E15}$$

Corollary 3: *For* $\omega_{\min} \geq 4$,

$$r_{\max}^{(aprx)} = \max\left(\left|R^{(aprx)}\right|\right) \leq 3/2. \tag{E16}$$

Corollary 4: *For* $\alpha\Gamma^2 \geq 4\log n + \omega_{\min} + 2$ *and* $\omega_{\min} \geq 4$,

$$r_{\max} = \max\left(|R|\right) \leq r_{\max}^{(aprx)} + r_{\max}^{(neg)} \leq 2. \tag{E17}$$

Define $T^{(\mathrm{neg})} = T - T^{(\mathrm{block})}$. Similarly, define $U^{(\mathrm{neg})} = U - U^{(\mathrm{block})}$. The following lemma bounds these coefficients.

Lemma 9: *For* $\beta \geq \alpha \geq 1$ *and* $\alpha\Gamma^2 \geq 64$,

$$t_{\max} = \max\left(|T|\right) \leq \frac{3}{2}\beta, \tag{E18}$$

$$t_{\max}^{(neg)} = \max\left(\left|T^{(neg)}\right|\right) \leq \beta \exp\left(-\alpha\Gamma^2/4\right), \tag{E19}$$

$$u_{\max} = \max\left(|U|\right) \leq 2\beta^3, \tag{E20}$$

$$u_{\max}^{(neg)} = \max\left(\left|U^{(neg)}\right|\right) \leq 2\beta^3/\Gamma. \tag{E21}$$

Proofs of the technical lemmas follow the proof of Lemma 1. Note that the conditions of the technical lemmas (and corollaries) are implied by the conditions of Lemma 1.

Lemma 10: (restated). *If* $\beta \geq \alpha \geq 1$, $\omega_{\min} \geq 4$, $\Gamma \geq 640n^{18}\beta^3$, *and* $\alpha\Gamma^2 \geq 12\log\beta + 80\log n + 4\omega_{\min} + 24$, *then*

$$\left\|H^{(ES)} - H^{(round)}\right\| \leq 3n^2\alpha f\left(\omega_{\min}\right) + \frac{1}{20n^2} + 8n^4\sqrt{\alpha}\cdot\exp(-\omega_{\min}/2), \tag{46a}$$

where $\omega_{\min} = \alpha\gamma_{\min}^2$.

Proof of Lemma 1. We bound the kinetic and potential parts separately, starting with the former.

Define $\tilde{T}^{(\mathrm{aprx})} = R^{(\mathrm{aprx})}T^{(\mathrm{block})}R^{(\mathrm{aprx})}$, and recall that $\tilde{T} = RTR$. The first task is to bound the error of approximating $\tilde{T}$ by $\tilde{T}^{(\mathrm{aprx})}$:

$$\max\left(\left|\tilde{T} - \tilde{T}^{(\mathrm{aprx})}\right|\right) = \max\left(\left|RTR - R^{(\mathrm{aprx})}T^{(\mathrm{block})}R^{(\mathrm{aprx})}\right|\right) \tag{E22}$$

$$\leq \max\left(\left|RTR - RT^{(\mathrm{block})}R\right|\right) + \max\left(\left|RT^{(\mathrm{block})}R - R^{(\mathrm{aprx})}T^{(\mathrm{block})}R^{(\mathrm{aprx})}\right|\right). \tag{E23}$$

We bound each term from Eq. (E23) separately. We use the fact that if A and B are $m \times m$ matrices, then $\max(|AB|) \leq m \cdot \max(|A|) \cdot \max(|B|)$. Since the matrices R and T are $n(d+1) \times n(d+1)$ matrices and $d+1 \leq n$, we pick up a factor of at most n^2 every time this rule is applied:

$$\max\left(\left|RTR - RT^{(\mathrm{block})}R\right|\right) = \max\left(\left|R(T - T^{(\mathrm{block})})R\right|\right) \tag{E24}$$

$$\leq n^4(r_{\max})^2\max(|T - T^{(\mathrm{block})}|) = n^4(r_{\max})^2 t_{\max}^{(\mathrm{neg})} \tag{E25}$$

$$\leq 4n^2\beta\exp(-\alpha\Gamma^2/4). \tag{E26}$$

The last inequality uses the bound from Eq. (E17) that $r_{\max} \leq 2$ and from Eq. (E19) that $t_{\max}^{(\mathrm{neg})} \leq \beta\exp(-\alpha\Gamma^2/4)$. To bound the second term from Eq. (E23), recall that $R = R^{(\mathrm{aprx})} + R^{(\mathrm{neg})}$:

$$\max\left(\left|RT^{(\mathrm{block})}R - R^{(\mathrm{aprx})}T^{(\mathrm{block})}R^{(\mathrm{aprx})}\right|\right) \tag{E27}$$

$$= \max\left\{\left|\left[R^{(\mathrm{aprx})} + R^{(\mathrm{neg})}\right]T^{(\mathrm{block})}\left[R^{(\mathrm{aprx})} + R^{(\mathrm{neg})}\right] - R^{(\mathrm{aprx})}T^{(\mathrm{block})}R^{(\mathrm{aprx})}\right|\right\} \tag{E28}$$

$$= \max\left(\left|R^{(\mathrm{aprx})}T^{(\mathrm{block})}R^{(\mathrm{neg})} + R^{(\mathrm{neg})}T^{(\mathrm{block})}R^{(\mathrm{aprx})} + R^{(\mathrm{neg})}T^{(\mathrm{block})}R^{(\mathrm{neg})}\right|\right) \tag{E29}$$

$$\leq n^4 t_{\max} r_{\max}^{(\mathrm{neg})}\left(2r_{\max}^{(\mathrm{aprx})} + r_{\max}^{(\mathrm{neg})}\right) \tag{E30}$$

$$\leq n^4 \times \underbrace{\frac{3}{2}\beta}_{\text{Eq. (E18)}} \times \underbrace{\exp\left[-(\alpha\Gamma^2 - \omega_{\min})/2\right]}_{\text{Eq. (E5)}}\left[\left(2 \times \underbrace{\frac{3}{2}}_{\text{Eq. (E16)}}\right) + \underbrace{\frac{1}{2}}_{\text{Eq. (E6)}}\right] \tag{E31}$$

$$\leq 6n^4\beta\exp\left[-(\alpha\Gamma^2 - \omega_{\min})/2\right] \leq 6n^4\beta\exp(-\alpha\Gamma^2/4). \tag{E32}$$

The last inequality is implied by the assumptions of the lemma, specifically that $\alpha\Gamma^2 \geq 2\omega_{\min}$. Putting together the bounds from Eqs. (E26) and (E32), we obtain that

$$\max\left(\left|\tilde{T} - \tilde{T}^{(\text{aprx})}\right|\right) \leq 10n^4\beta\exp(-\alpha\Gamma^2/4). \tag{E33}$$

The next step is to use the approximation for the kinetic-energy terms for the primitive orbitals to obtain the kinetic-energy term for the composite orbitals. Recall that composite orbital ϕ_i is a superposition of $\phi_{i,p}$:

$$\phi_i = \sum_{p=0}^{d} \psi_p \phi_{i,p},$$

where $\psi_0 = 1/\sqrt{2}$ and $\psi_{p>0} = 1/\sqrt{2d}$. Therefore, the kinetic-energy terms for the composite orbitals are just superpositions of the kinetic-energy terms for the primitive orbitals:

$$t_{i,j} = \sum_{p,q} \psi_p \psi_q t_{(i,p),(j,q)}.$$

We can apply this principle to $\tilde{T}$ and $\tilde{T}^{(\text{aprx})}$ as well:

$$\tilde{t}_{i,j} = \sum_{p,q} \psi_p \psi_q \tilde{t}_{(i,p),(j,q)} \quad \text{and} \quad \tilde{t}^{(\text{aprx})}_{i,j} = \sum_{p,q} \psi_p \psi_q \tilde{t}^{(\text{aprx})}_{(i,p),(j,q)}.$$

Using the bound from Eq. (E33),

$$\begin{aligned} |\tilde{t}_{i,j} - \tilde{t}^{(\text{aprx})}_{i,j}| &\leq \sum_{p,q} \psi_p \psi_q |\tilde{t}_{(i,p),(j,q)} - \tilde{t}^{(\text{aprx})}_{(i,p),(j,q)}| && \text{(E34)} \\ &\leq \frac{1}{2}(d+1)^2 \max\left(\left|\tilde{T} - \tilde{T}^{(\text{aprx})}\right|\right) \\ &\leq 5n^6\beta\exp(-\alpha\Gamma^2/4). && \text{(E35)} \end{aligned}$$

The next task is to bound $|\tilde{t}^{(\text{aprx})}_{i,j} - t^{(\text{round})}_{i,j}|$. We consider three separate cases. In each case, we show that

$$\left|\tilde{t}^{(\text{aprx})}_{i,j} - t^{(\text{round})}_{i,j}\right| \leq \alpha f(\omega_{\min}). \tag{E36}$$

Recall that $\tilde{T}^{(\text{aprx})} = R^{(\text{aprx})} T^{(\text{block})} R^{(\text{aprx})}$, so matrix $\tilde{T}^{(\text{aprx})}$ is block diagonal. This means that $\tilde{t}^{(\text{aprx})}_{(i,p),(j,q)} = 0$ unless $(i,p) = (j,q)$ or $\{i,j\} \in E$ and $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$. This considerably simplifies the sum

$$\tilde{t}^{(\text{aprx})}_{i,j} = \sum_{p,q} \psi_p \psi_q \tilde{t}^{(\text{aprx})}_{(i,p),(j,q)}. \tag{E37}$$

a. Case 1 Diagonal element: $i = j$. First note that if $p = 0$ or $p > \deg_i$, then the block containing (i,p) is just the single entry on the diagonal. In this case, $r^{(\text{aprx})}_{(i,p),(i,p)} = 1$ and $\tilde{t}^{(\text{aprx})}_{(i,p),(i,p)} = t_{(i,p),(i,p)}$.

Thus, when $i = j$, the sum given in Eq. (E37) simplifies to

$$\begin{aligned} \tilde{t}^{(\text{aprx})}_{i,i} &= \frac{1}{2} t_{(i,0),(i,0)} + \frac{1}{2d} \sum_{j:\{i,j\}\in E} \text{ON}\left(R^{(\text{aprx})}_{i,j} T_{i,j} R^{(\text{aprx})}_{i,j}\right) \\ &\quad + \frac{1}{2d} \sum_{p>\deg_i} t_{(i,p),(i,p)}. && \text{(E38)} \end{aligned}$$

The function t is defined in Eq. (C11), so that $t_\beta(0) = t_{(i,0),(i,0)}$ and $t_\alpha(0) = t_{(i,p),(i,p)}$ for $p > 0$. Thus,

$$\begin{aligned} \tilde{t}^{(\text{aprx})}_{i,i} &= \frac{1}{2} t_\beta(0) + \frac{1}{2d} \sum_{j:\{i,j\}\in E} \text{ON}\left(R^{(\text{aprx})}_{i,j} T_{i,j} R^{(\text{aprx})}_{i,j}\right) \\ &\quad + \frac{1}{2d} \sum_{p>\deg_i} t_\alpha(0). && \text{(E39)} \end{aligned}$$

Recall from Eq. (C31) that the diagonal coefficients of $T^{(\text{round})}$ are

$$t^{(\text{round})}_{i,i} = c_T = \frac{1}{2}\left[t_\beta(0) + t_\alpha(0)\right] = \frac{1}{2} t_\beta(0) + \frac{1}{2d} \sum_{p>0} t_\alpha(0). \tag{E40}$$

Therefore, the difference between $\tilde{t}^{(\text{aprx})}_{i,j}$ and $t^{(\text{round})}_{i,j}$ is

$$\begin{aligned} &\left|\tilde{t}^{(\text{aprx})}_{i,i} - t^{(\text{round})}_{i,i}\right| \\ &\quad = \left|\frac{1}{2d} \sum_{j:\{i,j\}\in E} \text{ON}\left(R^{(\text{aprx})}_{i,j} T_{i,j} R^{(\text{aprx})}_{i,j}\right) - t_\alpha(0)\right| && \text{(E41)} \\ &\quad \leq \frac{1}{2d} \sum_{j:\{i,j\}\in E} \left|\text{ON}\left(R^{(\text{aprx})}_{i,j} T_{i,j} R^{(\text{aprx})}_{i,j}\right) - t_\alpha(0)\right| && \text{(E42)} \\ &\quad \leq \frac{1}{2d} \sum_{j:\{i,j\}\in E} \alpha\omega_{i,j}\epsilon^2_{i,j} \quad \text{by Eq. (E13)} && \text{(E43)} \\ &\quad \leq \frac{\alpha}{2d} \sum_{j:\{i,j\}\in E} f(\omega_{i,j}) && \text{(E44)} \\ &\quad \leq \frac{\alpha}{2d} d f(\omega_{\min}) \quad \omega_{\min} \geq 2 && \text{(E45)} \\ &\quad = \frac{\alpha}{2} f(\omega_{\min}) \leq \alpha f(\omega_{\min}). && \text{(E46)} \end{aligned}$$

Note that since $\omega_{\min} \geq 2$ (by the assumptions of the lemma), the function $f(\omega) = \omega^2\exp(-\omega)$ is maximized at $\omega_{\min}$.

b. Case 2 Off-diagonal element corresponding to edge: $\{i,j\} \in E$. In this case, there is exactly one p and exactly one q such that (i,p) and (j,q) are in the same block, where

$\mathcal{B}(i,j) = \{(i,p),(j,q)\}$. Thus, the summation in Eq. (E37) has only one nonzero term:

$$\tilde{t}_{i,j}^{(\mathrm{aprx})} = \frac{1}{2d}\mathrm{OFF}\left(R_{i,j}^{(\mathrm{aprx})} T_{i,j} R_{i,j}^{(\mathrm{aprx})}\right). \tag{E47}$$

Recall from Eq. (C32) that $t_{i,j}^{(\mathrm{round})} = -\alpha/4d\sqrt{f(\omega_{i,j})}$.

Therefore,

$$\left|\tilde{t}_{i,j}^{(\mathrm{aprx})} - t_{i,j}^{(\mathrm{round})}\right| = \frac{1}{2d}\left|\mathrm{OFF}\left(R_{i,j}^{(\mathrm{aprx})} T_{i,j} R_{i,j}^{(\mathrm{aprx})}\right) - \left[-\frac{\alpha}{2}\sqrt{f(\omega_{i,j})}\right]\right| \tag{E48}$$

$$\leq \frac{1}{2d}\frac{\alpha}{2}\sqrt{f(\omega_{i,j})}4\epsilon_{i,j}^2 \quad \text{by Eq. } (E14) \tag{E49}$$

$$= \frac{\alpha}{d}\omega_{i,j}\exp(-3\omega_{i,j}/2) \tag{E50}$$

$$\leq \alpha\omega_{i,j}\exp(-\omega_{i,j}) \tag{E51}$$

$$\leq \alpha f(\omega_{\min}). \tag{E52}$$

Again, we are using the fact that since $\omega_{\min} \geq 2$, the function $f(\omega) = \omega^2\exp(-\omega)$ is maximized at $\omega_{\min}$.

c. Case 3. Off-diagonal element corresponding to nonedge: $\{i,j\} \notin E$. In this case, (i,p) and (j,q) are in different blocks for all p,q, and so the summation in Eq. (E37) is empty. That is, $\tilde{t}_{i,j}^{(\mathrm{aprx})} = 0$. Recall that $t_{i,j}^{(\mathrm{round})}$ is also zero for $\{i,j\} \notin E$.

Finally, we can combine the bound for $\left|\tilde{t}_{i,j} - \tilde{t}_{i,j}^{(\mathrm{aprx})}\right|$ from Eq. (E35) and the bound for $\left|\tilde{t}_{i,j}^{(\mathrm{aprx})} - t_{i,j}^{(\mathrm{round})}\right|$ from Eq. (E36):

$$\left\|T^{(\mathrm{ES})} - T^{(\mathrm{round})}\right\| \leq \left\|\sum_{\substack{i,j\\ \sigma}}\left(\tilde{t}_{i,j} - t_{i,j}^{(\mathrm{round})}\right)\tilde{a}_{i,\sigma}^\dagger\tilde{a}_{j,\sigma}\right\| \tag{E53}$$

$$\leq \sum_{\substack{i,j\\ \sigma}}\left|\tilde{t}_{i,j} - t_{i,j}^{(\mathrm{round})}\right|\left\|\tilde{a}_{i,\sigma}^\dagger\tilde{a}_{j,\sigma}\right\| = 2\sum_{i,j}\left|\tilde{t}_{i,j} - t_{i,j}^{(\mathrm{round})}\right| \tag{E54}$$

$$\leq 2\sum_{i,j}\left|\tilde{t}_{i,j} - \tilde{t}_{i,j}^{(\mathrm{aprx})}\right| + 2\sum_{i,j}\left|\tilde{t}_{i,j}^{(\mathrm{aprx})} - t_{i,j}^{(\mathrm{round})}\right| \tag{E55}$$

$$\leq 10n^8\beta\exp(-\alpha\Gamma^2/4) + 2n^2\alpha f(\omega_{\min}). \tag{E56}$$

We can apply the conditions of the lemma to simplify this expression. The lower bound on $\alpha\Gamma^2$ implies that $\exp(-\alpha\Gamma^2/4) \leq (10n^6\beta)^{-1}\exp(-\omega_{\min})$. Using the assumptions that $\alpha \geq 1$ and $\omega_{\min} \geq 1$:

$$10n^8\beta\exp(-\alpha\Gamma^2/4) \leq n^2\exp(-\omega_{\min}) \leq n^2\alpha(\omega_{\min})^2\exp(-\omega_{\min}) = n^2\alpha f(\omega_{\min}).$$

Recall that $f(\omega) = \omega^2\exp(-\omega)$. The final bound for the kinetic-energy difference is

$$\left\|T^{(\mathrm{ES})} - T^{(\mathrm{round})}\right\| \leq 3n^2\alpha f(\omega_{\min}). \tag{E57}$$

Next, we consider the terms for the potential energy. As with the kinetic-energy terms, we approximate $\tilde{U} = (R\otimes R)U(R\otimes R)$ by

$$\tilde{U}^{(\mathrm{aprx})} = (R^{(\mathrm{aprx})}\otimes R^{(\mathrm{aprx})})\tilde{U}^{(\mathrm{block})}(R^{(\mathrm{aprx})}\otimes R^{(\mathrm{aprx})}). \tag{E58}$$

The matrices are now $n^2(d+1)^2 \times n^2(d+1)^2$. We use the fact that if A and B are $m\times m$ matrices, then $\max(|AB|) \leq m\max(|A|)\cdot\max(|B|)$. Since $d+1 \leq n$, we pick up a factor of at most n^4 every time this principle is applied. We bound $\max(|\tilde{U} - \tilde{U}^{(\mathrm{aprx})}|)$ in two stages. First, we bound

$$\max\left[\left|\tilde{U} - (R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R)\right|\right] = \max\left[\left|(R\otimes R)U(R\otimes R) - (R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R)\right|\right] \tag{E59}$$

$$= \max\left[\left|(R\otimes R)(U - \tilde{U}^{(\mathrm{block})})(R\otimes R)\right|\right] \tag{E60}$$

$$\leq n^8(r_{\max})^4 u_{\max}^{(\mathrm{neg})} \tag{E61}$$

$$\leq n^8 \underbrace{2^4}_{\text{Eq. } E17}\underbrace{2\beta^3/\Gamma}_{\text{Eq. } E21} = 32n^8\beta^3/\Gamma. \tag{E62}$$

The next step is to bound

$$\max\left[\left|(R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R) - \tilde{U}^{(\mathrm{aprx})}\right|\right] \tag{E63}$$

$$= \max\left[\left|(R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R) - (R^{(\mathrm{aprx})}\otimes R^{(\mathrm{aprx})})\tilde{U}^{(\mathrm{block})}(R^{(\mathrm{aprx})}\otimes R^{(\mathrm{aprx})})\right|\right]. \tag{E64}$$

If we substitute $R = R^{(\mathrm{neg})} + R^{(\mathrm{aprx})}$ in to the expression $(R\otimes R)U^{(\mathrm{block})}(R\otimes R)$ and expand the product, we obtain the sum of 2^4 terms:

$$(R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R) = \sum_{a,b,c,d\in\{\mathrm{neg},\mathrm{aprx}\}}(R^{(\mathrm{a})}\otimes R^{(\mathrm{b})})\tilde{U}^{(\mathrm{block})}(R^{(\mathrm{c})}\otimes R^{(\mathrm{d})}). \tag{E65}$$

In bounding the difference from Eq. (E64), we are left with the terms in which a,b,c,d are not all equal to "aprx," so

every remaining term has at least one factor of $R^{(\mathrm{neg})}$:

$$|(R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R)-\tilde{U}^{(\mathrm{aprx})}|$$

$$\le n^8 u_{\max}\sum_{x=0}^{3}\binom{4}{x}\left(r_{\max}^{(\mathrm{aprx})}\right)^x\left(r_{\max}^{(\mathrm{neg})}\right)^{4-x} \tag{E66}$$

$$\le n^8 u_{\max}\times 15\times r_{\max}^{(\mathrm{neg})}\left[\max\left\{r_{\max}^{(\mathrm{aprx})},r_{\max}^{(\mathrm{neg})}\right\}\right]^3 \tag{E67}$$

$$\le n^8 \underbrace{2\beta^3}_{\text{Eq. }(E20)}\times 15\times \underbrace{n^2\exp\left[-(\alpha\Gamma^2-\omega_{\min})/2\right]}_{\text{Eq. }(E5)}$$

$$\times \underbrace{\left(\frac{3}{2}\right)^3}_{\text{Eqs. }(E16)\text{ and }(E6)} \tag{E68}$$

$$\le 102n^{10}\beta^3\exp\left[-(\alpha\Gamma^2-\omega_{\min})/2\right] \tag{E69}$$

$$\le 102n^{10}\beta^3\exp(-\alpha\Gamma^2/4). \tag{E70}$$

The last inequality uses the assumption from the lemma that $\alpha\Gamma^2\ge 2\omega_{\min}$. Putting the two bounds from Eqs. (E62) and (E70) together, we obtain that

$$\max\left(\left|\tilde{U}-\tilde{U}^{(\mathrm{aprx})}\right|\right) \tag{E71}$$

$$\le \max\left[\left|\tilde{U}-(R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R)\right|\right]$$

$$+\max\left[\left|(R\otimes R)\tilde{U}^{(\mathrm{block})}(R\otimes R)-\tilde{U}^{(\mathrm{aprx})}\right|\right] \tag{E72}$$

$$\le 32n^8\beta^3/\Gamma+102n^{10}\beta^3\exp(-\alpha\Gamma^2/4). \tag{E73}$$

Since the composite orbitals are superpositions of the primitive orbitals, the potential-energy terms for the composite orbitals can be expressed as linear combinations of the potential-energy terms for the primitive orbitals. Therefore,

$$u_{i,j,k,l}=\sum_{p,q,r,s,\in[d+1]}\psi_p\psi_q\psi_r\psi_s u_{[(i,p),(j,q)][(l,r),(l,s)]}, \tag{E74}$$

where the amplitudes ψ are defined to be $\psi_0=1/\sqrt{2}$ and $\psi_{p>0}=1/\sqrt{2d}$. The same definition for $\tilde{u}_{i,j,k,l}$ and $\tilde{u}_{i,j,k,l}^{(\mathrm{aprx})}$ can be applied using the potential-energy terms for the primitive orbitals defined in $\tilde{U}$ and $\tilde{U}^{(\mathrm{aprx})}$. We can apply the bound from Eq. (E73) to bound the difference in the potential-energy terms for the composite orbitals:

$$|\tilde{u}_{i,j,k,l}-\tilde{u}_{i,j,k,l}^{(\mathrm{aprx})}|=\left|\sum_{p,q,r,s,\in[d+1]}\psi_p\psi_q\psi_r\psi_s\left(\tilde{u}_{[(i,p),(j,q)][(l,r),(l,s)]}-\tilde{u}^{(\mathrm{aprx})}_{[(i,p),(j,q)][(l,r),(l,s)]}\right)\right| \tag{E75}$$

$$\le\frac{1}{4}(d+1)^4\max\left(\left|\tilde{U}-\tilde{U}^{(\mathrm{aprx})}\right|\right) \tag{E76}$$

$$\le\frac{1}{4}n^4[32n^8\beta^3/\Gamma+102n^{10}\beta^3\exp(-\alpha\Gamma^2/4)] \tag{E77}$$

$$\le 8n^{12}\beta^3/\Gamma+26n^{14}\beta^3\exp(-\alpha\Gamma^2/4). \tag{E78}$$

We can now apply the assumptions of the lemma to simplify the above expression. The assumption that $\Gamma\ge 640n^{18}\beta^3$ implies that $8n^{12}\beta^3/\Gamma\le 1/(80n^6)$. The assumption that $\alpha\Gamma^2\ge 12\log\beta+80\log n+4\omega_{\min}+24\ge 12\log\beta+80\log n+40$ implies that $26n^{14}\beta^3\exp(-\alpha\Gamma^2/4)\le 1/(80n^6)$. Therefore,

$$8n^{12}\beta^3/\Gamma+26n^{14}\beta^3\exp(-\alpha\Gamma^2/4)\le\frac{1}{40n^6}. \tag{E79}$$

The next task is to bound $|\tilde{u}_{i,j,k,l}^{(\mathrm{aprx})}-u_{i,j,k,l}^{(\mathrm{round})}|$. Since

$$\tilde{U}^{(\mathrm{aprx})}=(R^{(\mathrm{aprx})}\otimes R^{(\mathrm{aprx})})\tilde{U}^{(\mathrm{block})}(R^{(\mathrm{aprx})}\otimes R^{(\mathrm{aprx})})$$

is block diagonal, many of the terms in the sum given in Eq. (E74) are zero. We consider three cases. In each case, we show that

$$|\tilde{u}_{i,j,k,l}^{(\mathrm{aprx})}-\tilde{u}_{i,j,k,l}^{(\mathrm{round})}|\le 4\sqrt{\alpha}\exp\left(-\omega_{\min}/2\right). \tag{E80}$$

d. Case 1 On-site term $i=j=k=l$. Note that the entry in row $[(i,p),(i,q)]$ and row $[(i,r),(i,s)]$ is outside of a block unless $p=q=r=s$. If $p=0$ or $p>\deg_i$, then the block containing $[(i,p),(i,p)]$ is just the single entry on the diagonal. In this case, $r^{(\mathrm{aprx})}_{(i,p),(i,p)}\otimes r^{(\mathrm{aprx})}_{(i,p),(i,p)}=1$ and the diagonal element at $[(i,p),(i,p)]$ is the same for $\tilde{U}^{(\mathrm{aprx})}$ and U.

If $p = 0$, then primitive orbital $\phi_{i,0}$ is a Gaussian of width β and the diagonal term of U at $[(i,0),(i,0)]$ is as in Eq. (C14) defined as $u_\beta^{(\mathrm{Coul})}(0)$. For $p > \deg_i$, then primitive orbital $\phi_{i,p}$ is a Gaussian of width α and the diagonal term of U at $[(i,p),(i,p)]$ is, as in Eq. (C14), defined as $u_\alpha^{(\mathrm{Coul})}(0)$.

Thus, when $i = j = k = l$, the sum given in Eq. (E74) simplifies to

$$\tilde{u}_{i,i,i,i}^{(\mathrm{aprx})} = \frac{1}{4d^2} \sum_{0<p\le \deg_i} \left[\left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} \right]_{(i,p),(i,p),(i,p),(i,p)} \tag{E81}$$

$$+ \frac{1}{4} u_\beta^{(\mathrm{Coul})}(0) + \frac{1}{4d^2} \sum_{p>\deg_i} u_\alpha^{(\mathrm{Coul})}(0). \tag{E82}$$

Recall that $u_{i,i,i,i}^{(\mathrm{round})}$ is defined in Eq. (C41) to be

$$c_U^{(\mathrm{round})} = \frac{1}{4} u_\beta^{(\mathrm{Coul})}(0) + \frac{1}{4d} u_\alpha^{(\mathrm{Coul})}(0) = \frac{1}{4} u_\beta^{(\mathrm{Coul})}(0) + \frac{1}{4d^2} \sum_{p\in[d]} u_\alpha^{(\mathrm{Coul})}(0) \tag{E83}$$

Therefore,

$$\left| \tilde{u}_{i,i,i,i}^{(\mathrm{aprx})} - u_{i,i,i,i}^{(\mathrm{round})} \right| \tag{E84}$$

$$= \frac{1}{4d^2} \left| \sum_{0<p\le\deg_i} \left\{ \left[\left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} \right]_{(i,p),(i,p),(i,p),(i,p)} \right\} - u_\alpha^{(\mathrm{Coul})}(0) \right| \tag{E85}$$

$$= \frac{1}{4d^2} \left| \sum_{0<p\le\deg_i} \left[\left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} - U_{i,j} \right]_{(i,p),(i,p),(i,p),(i,p)} \right| \tag{E86}$$

$$\le \frac{1}{4d^2} \cdot d \cdot \max \left| \left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} - U_{i,j} \right| \tag{E87}$$

$$\le \frac{1}{4} \underbrace{16\sqrt{\alpha}\epsilon_{\max}}_{(E15)} = 4\sqrt{\alpha}\exp(-\omega_{i,j}/2) \le 4\sqrt{\alpha}\exp(-\omega_{\min}/2). \tag{E88}$$

The last inequality uses the assumption of the lemma that $\omega_{\min} \ge 2$.

e. Case 2 All indices within block corresponding to edge $\{i,j\} \in E$. Let $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$.

Consider, for example, the term $\tilde{u}_{i,j,j,i}^{(\mathrm{aprx})}$. The sum in Eq. (E74) has only one nonzero term corresponding to row $[(i,p),(j,q)]$ and column $[(j,q),(i,p)]$. So

$$\tilde{u}_{i,j,j,i}^{(\mathrm{aprx})} = \frac{1}{4d^2} \left[\left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{block})}\right)^{\otimes 2} \right]_{[(i,p),(j,q)],[(j,q),(i,p)]}. \tag{E89}$$

Recall that

$$u_{i,j,j,i}^{(\mathrm{round})} = \frac{1}{4d^2} u_\alpha^{(\mathrm{Coul})}(\gamma_{i,j}) = \frac{1}{4d^2} u_{[(i,p),(j,q)],[(j,q),(i,p)]}. \tag{E90}$$

The first equality comes from the definition of $u^{(\mathrm{round})}$ in Eq. (C42) and the second comes from the definition of $u_\alpha^{(\mathrm{Coul})}(\gamma_{i,j})$ in Eq. (C14). The entry in row $[(i,p),(j,q)]$ and column $[(j,q),(i,p)]$ is inside the block corresponding to edge $\{i,j\}$.

Therefore,

$$\left|\tilde{u}^{(\mathrm{aprx})}_{i,j,j,i} - u^{(\mathrm{round})}_{i,j,j,i}\right| = \frac{1}{4d^2}\max\left[\left|\left(R^{(\mathrm{block})}_{i,j}\right)^{\otimes 2} U_{i,j}\left(R^{(\mathrm{block})}_{i,j}\right)^{\otimes 2} - U_{i,j}\right|\right] \tag{E91}$$

$$\leq \frac{1}{4}\underbrace{16\sqrt{\alpha}\epsilon_{i,j}}_{\text{Eq. }(E15)} = 4\sqrt{\alpha}\exp(-\omega_{i,j}/2) \leq 4\sqrt{\alpha}\exp(-\omega_{\min}/2). \tag{E92}$$

The same bound holds for $\left|\tilde{u}^{(\mathrm{aprx})}_{i,i,j,i} - u^{(\mathrm{round})}_{i,i,j,i}\right|$, $\left|\tilde{u}^{(\mathrm{aprx})}_{j,i,j,i} - u^{(\mathrm{round})}_{j,i,j,i}\right|$, etc. for $\{i,j\} \in E$.

f. Case 3 At least one pair of indices corresponding to nonedge $\{i,j\} \notin E$. In this case, both $\tilde{u}^{(\mathrm{aprx})}_{i,j,k,l}$ and $u^{(\mathrm{round})}_{i,j,k,l}$ are zero. All together,

$$\left\|U^{(\mathrm{ES})} - U^{(\mathrm{round})}\right\| \leq \left\|\frac{1}{2}\sum_{\substack{i,j,k,l\\ \sigma,\tau}}\left(\tilde{u}_{i,j,k,l} - u^{(\mathrm{round})}_{i,j,k,l}\right)\tilde{a}^\dagger_{i,\sigma}\tilde{a}^\dagger_{j,\sigma}\tilde{a}_{k,\sigma}\tilde{a}_{l,\sigma}\right\| \tag{E93}$$

$$\leq \frac{1}{2}\sum_{\substack{i,j,k,l\\ \sigma,\tau}}\left|\tilde{u}_{i,j,k,l} - u^{(\mathrm{round})}_{i,j,k,l}\right|\left\|\tilde{a}^\dagger_{i,\sigma}\tilde{a}^\dagger_{j,\sigma}\tilde{a}_{k,\sigma}\tilde{a}_{l,\sigma}\right\| \tag{E94}$$

$$= \frac{1}{2}\times\underbrace{4}_{\sigma,\tau}\sum_{i,j,k,l}\left|\tilde{u}_{i,j,k,l} - u^{(\mathrm{round})}_{i,j,k,l}\right| \tag{E95}$$

$$\leq 2\sum_{i,j,k,l}\left|\tilde{u}_{i,j,k,l} - \tilde{u}^{(\mathrm{aprx})}_{i,j,k,l}\right| + 2\sum_{i,j,k,l}\left|\tilde{u}^{(\mathrm{aprx})}_{i,j,k,l} - u^{(\mathrm{round})}_{i,j,k,l}\right| \tag{E96}$$

$$\leq 2n^4\underbrace{\left(\frac{1}{40n^6}\right)}_{\text{Eq. }(E79)} + 2n^4\times\underbrace{4\sqrt{\alpha}\exp(-\omega_{\min}/2)}_{\text{Eq. }(E80)} \tag{E97}$$

$$= \frac{1}{20n^2} + 8n^4\sqrt{\alpha}\exp(-\omega_{\min}/2). \tag{E98}$$

Equations (E57) and (E98) imply the lemma:

$$\left\|H^{(\mathrm{ES})} - H^{(\mathrm{round})}\right\| \leq \left\|T^{(\mathrm{ES})} - T^{(\mathrm{round})}\right\| + \left\|U^{(\mathrm{ES})} - U^{(\mathrm{round})}\right\| \tag{E99}$$

$$\leq 3n^2\alpha f\left(\omega_{\min}\right) + \frac{1}{20n^2} + 8n^4\sqrt{\alpha}\exp(-\omega_{\min}/2). \tag{E100}$$

■

1. Proof of Lemma 7

Define $\epsilon_{\max}$ to be the largest off-diagonal element of S and ϵ_{neg} to be the largest entry of $S^{(\mathrm{neg})}$, which is the largest entry of S outside of an edge block:

$$\epsilon_{\max} = \max_{(i,p)\neq(j,q)} s_{(i,p),(j,q)} = s_\alpha(\gamma_{\min}) = \exp(-\omega_{\min}/2), \tag{E101}$$

$$\epsilon_{\mathrm{neg}} = \max\left(S^{(\mathrm{neg})}\right) \leq s_\alpha(\Gamma) = \exp(-\alpha\Gamma^2/2). \tag{E102}$$

Let $S^{(\mathrm{block})} = I + S^{(\mathrm{OD})}$; $S^{(\mathrm{OD})}$ has at most one entry per row or column, and that entry is between 0 and $\epsilon_{\max}$. Using the Taylor expansion

$$M^{-1/2} = \sum_{k=0}^{\infty}(-2)^{-k}\frac{(2k-1)!!}{k!}(M-I)^k \tag{E103}$$

of a matrix M around the identity I, we have

$$R^{(\mathrm{neg})} = R - R^{(\mathrm{aprx})} \tag{E104}$$

$$= (S)^{-1/2} - \left(S^{(\mathrm{block})}\right)^{-1/2} \tag{E105}$$

$$= \left(I + S^{(\mathrm{OD})} + S^{(\mathrm{neg})}\right)^{-1/2} - \left(I + S^{(\mathrm{OD})}\right)^{-1/2} \tag{E106}$$

$$= \sum_{k=0}^{\infty} (-2)^{-k} \frac{(2k-1)!!}{k!} \left[\left(S^{(\mathrm{OD})} + S^{(\mathrm{neg})}\right)^{k} - \left(S^{(\mathrm{OD})}\right)^{k}\right]. \tag{E107}$$

Entry-wise,

$$\left[\left(S^{(\mathrm{OD})} + S^{(\mathrm{neg})}\right)^{k}\right]_{(i_0,l_0),(i_k,l_k)} \tag{E108}$$

$$= \sum_{(i_1,l_1),\ldots,(i_{k-1},l_{k-1})} \left(S^{(\mathrm{OD})} + S^{(\mathrm{neg})}\right)_{(i_0,l_0),(i_1,l_1)} \cdots \left(S^{(\mathrm{OD})} + S^{(\mathrm{neg})}\right)_{(i_{k-1},l_{k-1}),(i_k,l_k)} \tag{E109}$$

$$= \sum_{0<\left\|\mathbf{x}_{i_{k'},l_{k'}} - \mathbf{x}_{i_{k'+1},l_{k'+1}}\right\|} s_{(i_0,l_0),(i_1,l_1)} \cdots s_{(i_{k-1},l_{k-1}),(i_k,l_k)}, \tag{E110}$$

where the summation excludes the diagonal entries. (Recall that I, $S^{(\mathrm{OD})}$, and $S^{(\mathrm{neg})}$ have disjoint support.) Similarly,

$$\left[\left(S^{(\mathrm{OD})}\right)^{k}\right]_{(i_0,l_0),(i_k,l_k)} = \sum_{0<\left\|\mathbf{x}_{i_{k'},l_{k'}} - \mathbf{x}_{i_{k'+1},l_{k'+1}}\right\|<\Gamma} s_{(i_0,l_0),(i_1,l_1)} \cdots s_{(i_{k-1},l_{k-1}),(i_k,l_k)}, \tag{E111}$$

where the summation excludes both the diagonal and anything outside of the blocks. The difference between Eqs. (E110) and (E111) is the summation in Eq. (E110) restricted to when at least one of the neighboring pairs is at least Γ separated. Each term with exactly x pairs separated by at least Γ contributes at most $\epsilon_{\max}^{k-x}\epsilon_{\mathrm{neg}}^{x}$. There are $\binom{k}{x}$ places in the sequence that these pairs can occur. For each factor contributing more than ϵ_{neg} there is at most one index value $(i_{k'}, l_{k'})$, and for each factor contributing at most ϵ_{neg} there are at most $n(d+1) - 1 \leq 2n^2$ indices. Therefore,

$$\left[\left(S^{(\mathrm{OD})} + S^{(\mathrm{neg})}\right)^{k} - \left(S^{(\mathrm{OD})}\right)^{k}\right]_{(i_0,l_0),(i_k,l_k)} \tag{E112}$$

$$\leq \sum_{x=1}^{k} \binom{k}{x} \left(2n^2\epsilon_{\mathrm{neg}}\right)^{x} \epsilon_{\max}^{k-x} \tag{E113}$$

$$= \sum_{x=0}^{k-1} \binom{k}{x} \left(2n^2\epsilon_{\mathrm{neg}}\right)^{k-x} \epsilon_{\max}^{x} = \left(2n^2\epsilon_{\mathrm{neg}}\right)^{k} \sum_{x=0}^{k-1} \frac{k}{k-x} \binom{k-1}{x} \left(\frac{\epsilon_{\max}}{2n^2\epsilon_{\mathrm{neg}}}\right)^{x} \tag{E114}$$

$$\leq \left(2n^2\epsilon_{\mathrm{neg}}\right)^{k} \sum_{x=0}^{k-1} k \binom{k-1}{x} \left(\frac{\epsilon_{\max}}{2n^2\epsilon_{\mathrm{neg}}}\right)^{x} = k\left(2n^2\epsilon_{\mathrm{neg}}\right)^{k} \left(1 + \frac{\epsilon_{\max}}{2n^2\epsilon_{\mathrm{neg}}}\right)^{k-1} \tag{E115}$$

$$= k\left(2n^2\epsilon_{\mathrm{neg}}\right)\left(2n^2\epsilon_{\mathrm{neg}} + \epsilon_{\max}\right)^{k-1} \tag{E116}$$

$$\leq k\left(2n^2\epsilon_{\mathrm{neg}}\right)\left(2\epsilon_{\max}\right)^{k-1} = kn^2 \frac{\epsilon_{\mathrm{neg}}}{\epsilon_{\max}} \left(2\epsilon_{\max}\right)^{k}, \tag{E117}$$

where we use the fact that

$$2n^2\epsilon_{\mathrm{neg}} = 2n^2 e^{-\alpha\Gamma^2/2} \leq e \cdot n^2 e^{-\alpha\Gamma^2/2} \leq e \cdot n^2 e^{-(4\log n + \omega_{\min} + 2)/2} = e^{-\omega_{\min}/2} = \epsilon_{\max} \tag{E118}$$

by assumption. Returning to the expression in Eq. (E107), the norm of each entry of $R^{(\mathrm{neg})}$ is then

$$\left|r^{(\mathrm{neg})}_{(i_0,l_0),(i_k,l_k)}\right| = \left|\sum_{k=0}^{\infty}(-2)^{-k}\frac{(2k-1)!!}{k!}\left[\left(S^{(\mathrm{OD})}+S^{(\mathrm{neg})}\right)^k-\left(S^{(\mathrm{OD})}\right)^k\right]_{(i_0,l_0),(i_k,l_k)}\right| \tag{E119}$$

$$\leq \sum_{k=0}^{\infty}(2)^{-k}\frac{(2k-1)!!}{k!}\left|\left[\left(S^{(\mathrm{OD})}+S^{(\mathrm{neg})}\right)^k-\left(S^{(\mathrm{OD})}\right)^k\right]_{(i_0,l_0),(i_k,l_k)}\right| \tag{E120}$$

$$\leq n^2\frac{\epsilon_{\mathrm{neg}}}{\epsilon_{\max}}\sum_{k=1}^{\infty}(2)^{-k}\frac{(2k-1)!!}{k!}k(2\epsilon_{\max})^k \tag{E121}$$

$$= n^2\frac{\epsilon_{\mathrm{neg}}}{\epsilon_{\max}}\sum_{k=1}^{\infty}\frac{(2k-1)!!}{(k-1)!}\epsilon^k_{\max} \tag{E122}$$

$$= n^2\frac{\epsilon_{\mathrm{neg}}}{\epsilon_{\max}}\frac{\epsilon_{\max}}{(1-2\epsilon_{\max})^{3/2}} \tag{E123}$$

$$\leq n^2\frac{\epsilon_{\mathrm{neg}}}{\epsilon_{\max}} \quad \text{for } \omega_{\min}\geq 4 \tag{E124}$$

$$\leq n^2\exp\left[-(\alpha\Gamma^2-\omega_{\min})/2\right]. \tag{E125}$$

■

2. Proof of Lemma 8

In this proof, we use the following form of Taylor's theorem. ■

Theorem 2: (Taylor's theorem with remainder in Lagrange form [25]). *Let f be a $(n+1)$-times differentiable function in the region $[0,1]$. Then, for every $x\in[0,1]$, there is some $c\in[0,x]$ such that*

$$f(x)=\sum_{k=0}^{n}\frac{f^{(k)}(0)}{k!}x^k+\frac{f^{(n+1)}(c)}{(n+1)!}x^{n+1}. \tag{E126}$$

Note that $\omega_{\min}\geq 2$ implies that $\epsilon_{i,j}=e^{-\omega_{i,j}/2}\leq e^{-\omega_{\min}/2}\leq 1/e$.
We start with the bounds on the entries of $R^{(\mathrm{aprx})}$. Given the derivatives

$$\frac{d}{d\epsilon}\left(\frac{1}{\sqrt{1+\epsilon}}\pm\frac{1}{\sqrt{1-\epsilon}}\right)=\frac{1}{2}\left[-(1+\epsilon)^{-3/2}\pm(1-\epsilon)^{-3/2}\right], \tag{E127}$$

$$\frac{d^2}{d\epsilon^2}\left(\frac{1}{\sqrt{1+\epsilon}}\pm\frac{1}{\sqrt{1-\epsilon}}\right)=\frac{3}{4}\left[(1+\epsilon)^{-5/2}\pm(1-\epsilon)^{-5/2}\right], \tag{E128}$$

$$\frac{d^3}{d\epsilon^3}\left(\frac{1}{\sqrt{1+\epsilon}}\pm\frac{1}{\sqrt{1-\epsilon}}\right)=\frac{15}{8}\left[-(1+\epsilon)^{-7/2}\pm(1-\epsilon)^{-7/2}\right], \tag{E129}$$

Theorem 6 implies that

$$\frac{1}{\sqrt{1+\epsilon}}+\frac{1}{\sqrt{1-\epsilon}}=2+0+\frac{1}{2}\frac{3}{4}\left[(1+\epsilon')^{-5/2}+(1-\epsilon')^{-5/2}\right]\epsilon^2, \tag{E130}$$

$$\frac{1}{\sqrt{1+\epsilon}}-\frac{1}{\sqrt{1-\epsilon}}=0-\epsilon+0-\frac{1}{3!}\frac{15}{8}\left[(1+\epsilon')^{-7/2}+(1-\epsilon')^{-7/2}\right]\epsilon^3 \tag{E131}$$

for some $\epsilon' \in [0,\epsilon]$. For $0 \le \epsilon \le 1/e$, we have

$$2 \le \frac{1}{\sqrt{1+\epsilon}} + \frac{1}{\sqrt{1-\epsilon}} \le 2 + 2\epsilon^2, \tag{E132}$$

$$-\epsilon - 2\epsilon^3 \le \frac{1}{\sqrt{1+\epsilon}} - \frac{1}{\sqrt{1-\epsilon}} \le -\epsilon. \tag{E133}$$

Dividing by 2 and substituting $\epsilon = \epsilon_{i,j}$ implies Eqs. (E11) and (E12).

Now, let us turn to the entries of $R_{i,j}^{(\mathrm{aprx})} T_{i,j} R_{i,j}^{(\mathrm{aprx})}$. Let $\mathcal{B}(i,j) = \{(i,p),(j,q)\}$. To make the notation more concise within this proof, we refer to the diagonal elements of $R_{i,j}^{(\mathrm{aprx})}$ as $r_{ON} = r_{(i,p),(i,p)}^{(\mathrm{aprx})} = r_{(j,q),(j,q)}^{(\mathrm{aprx})}$ and the off-diagonal elements as $r_{OFF} = r_{(i,p),(j,q)}^{(\mathrm{aprx})} = r_{(j,q),(i,p)}^{(\mathrm{aprx})}$. Note that

$$(r_{ON})^2 + (r_{OFF})^2 = \frac{1}{4}\left[\left(\frac{1}{\sqrt{1+\epsilon_{i,j}}} + \frac{1}{\sqrt{1-\epsilon_{i,j}}}\right)^2 + \left(\frac{1}{\sqrt{1+\epsilon_{i,j}}} - \frac{1}{\sqrt{1-\epsilon_{i,j}}}\right)^2\right] \tag{E134}$$

$$= \frac{1}{2}\left(\frac{1}{1+\epsilon_{i,j}} + \frac{1}{1-\epsilon_{i,j}}\right) = \frac{1}{1-\epsilon_{i,j}^2} \tag{E135}$$

and

$$r_{ON} \cdot r_{OFF} = \frac{1}{4}\left(\frac{1}{\sqrt{1+\epsilon_{i,j}}} + \frac{1}{\sqrt{1-\epsilon_{i,j}}}\right)\left(\frac{1}{\sqrt{1+\epsilon_{i,j}}} - \frac{1}{\sqrt{1-\epsilon_{i,j}}}\right) \tag{E136}$$

$$= \frac{1}{4}\left(\frac{1}{1+\epsilon_{i,j}} - \frac{1}{1-\epsilon_{i,j}}\right) = -\frac{\epsilon_{i,j}}{2(1-\epsilon_{i,j}^2)}. \tag{E137}$$

The diagonal entries of $T_{i,j}$ are $t_{(i,p),(i,p)} = t_{(j,q),(j,q)} = t_\alpha(0)$ and the off-diagonal entries are $t_{(i,p),(j,q)} = t_{(j,q),(i,p)} = t_\alpha(\gamma_{i,j})$. Then, the diagonal of $R_{i,j}^{(\mathrm{aprx})} T_{i,j} R_{i,j}^{(\mathrm{aprx})}$ entry is

$$\mathrm{ON}\left(R_{i,j}^{(\mathrm{aprx})} T_{i,j} R_{i,j}^{(\mathrm{aprx})}\right) \tag{E138}$$

$$= \begin{pmatrix} r_{ON} & r_{OFF} \end{pmatrix} \begin{pmatrix} t_\alpha(0) & t_\alpha(\gamma_{i,j}) \\ t_\alpha(\gamma_{i,j}) & t_\alpha(0) \end{pmatrix} \begin{pmatrix} r_{ON} \\ r_{OFF} \end{pmatrix} \tag{E139}$$

$$= t_\alpha(0)\left[(r_{ON})^2 + (r_{OFF})^2\right] + 2t_\alpha(\gamma_{i,j}) r_{ON} r_{OFF} \tag{E140}$$

$$= \frac{t_\alpha(0)}{1-\epsilon_{i,j}^2} - \frac{t_\alpha(\gamma_{i,j})\epsilon_{i,j}}{1-\epsilon_{i,j}^2} \tag{E141}$$

$$= \left[t_\alpha(0) - s_\alpha(\gamma_{i,j}) t_\alpha(\gamma_{i,j})\right] \frac{1}{1-\epsilon_{i,j}^2} \tag{E142}$$

$$= \left[\frac{3}{2}\alpha - \frac{1}{2}\alpha(3-\omega_{i,j})\exp(-\omega_{i,j})\right] \frac{1}{1-\epsilon_{i,j}^2} \tag{E143}$$

$$= \left[\frac{3}{2}\alpha(1-\epsilon_{i,j}^2) + \frac{1}{2}\alpha\omega_{i,j}\epsilon_{i,j}^2\right] \frac{1}{1-\epsilon_{i,j}^2} \tag{E144}$$

$$= t_\alpha(0) + \frac{\alpha\omega_{i,j}\epsilon_{i,j}^2}{2(1-\epsilon_{i,j}^2)} \tag{E145}$$

and the off-diagonal entry of $R_{i,j}^{(\mathrm{aprx})} T_{i,j} R_{i,j}^{(\mathrm{aprx})}$ is

$$\mathrm{OFF}\left(R_{i,j}^{(\mathrm{aprx})} T_{i,j} R_{i,j}^{(\mathrm{aprx})}\right) \tag{E146}$$

$$= \begin{pmatrix} r_{ON} & r_{OFF} \end{pmatrix} \begin{pmatrix} t_\alpha(0) & t_\alpha(\gamma_{i,j}) \\ t_\alpha(\gamma_{i,j}) & t_\alpha(0) \end{pmatrix} \begin{pmatrix} r_{OFF} \\ r_{ON} \end{pmatrix} \tag{E147}$$

$$= 2t_\alpha(0) \cdot r_{ON} \cdot r_{OFF} + t_\alpha(\gamma_{i,j}) \left[(r_{ON})^2 + (r_{OFF})^2\right] \tag{E148}$$

$$= -\frac{t_\alpha(0)\epsilon_{i,j}}{1-\epsilon_{i,j}^2} + \frac{t_\alpha(\gamma_{i,j})}{1-\epsilon_{i,j}^2} \tag{E149}$$

$$= \left[t_\alpha(\gamma_{i,j}) - s_\alpha(\gamma_{i,j}) t_\alpha(0)\right] \frac{1}{1-\epsilon_{i,j}^2} \tag{E150}$$

$$= \left[\frac{1}{2}\alpha(3-\omega_{i,j})\exp(-\omega_{i,j}/2) - \frac{3}{2}\alpha\exp(-\omega_{i,j}/2)\right] \times \frac{1}{1-\epsilon_{i,j}^2} \tag{E151}$$

$$= -\frac{1}{2}\alpha\omega_{i,j}\exp(-\omega_{i,j}/2)\frac{1}{1-\epsilon_{i,j}^2} \tag{E152}$$

$$= -\frac{1}{2}\alpha\sqrt{f(\omega_{i,j})}\frac{1}{1-\epsilon_{i,j}^2}. \tag{E153}$$

Let us look at this factor $(1-\epsilon^2)^{-1}$. It is always at least 1 and its first two derivatives are

$$\frac{d}{d\epsilon}\left(\frac{1}{1-\epsilon^2}\right) = \frac{2\epsilon}{\left(1-\epsilon^2\right)^2}, \tag{E154}$$

$$\frac{d^2}{d\epsilon^2}\left(\frac{1}{1-\epsilon^2}\right) = \frac{2(1+3\epsilon^2)}{\left(1-\epsilon^2\right)^3}. \tag{E155}$$

By Theorem 6,

$$\frac{1}{1-\epsilon^2} = 1 + \frac{(1+3\epsilon'^2)}{\left(1-\epsilon'^2\right)^3}\epsilon^2 \tag{E156}$$

for some $0 \le \epsilon' \le \epsilon$. For $\epsilon \le 1/e$, we have

$$1 \le \frac{1}{1-\epsilon^2} \le 1 + 4\epsilon^2 \le 2. \tag{E157}$$

The combination of Eqs. (E145), (E153), and (E157) implies Eqs. (E13) and (E14).

Finally, we turn to the bound for

$$\max\left|\left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} - U_{i,j}\right|.$$

Each entry of $\left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2}$ is a product of two terms from $\{r_{ON}, r_{OFF}\}$ and only the diagonal terms are $(r_{ON})^2$. For notational ease, we index the four rows and columns of $U_{i,j}$ by $\{0,1,2,3\}$. For $a,b \in \{0,1,2,3\}$, we denote the entry in row a and column b by $U_{i,j}[a,b]$. Now consider a particular entry in row a and column b of $\left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2}$. This entry is the sum of 16 terms, each of which is a product of one entry from $U_{i,j}$ and four factors from $\{r_{ON}, r_{OFF}\}$. The only term that has four factors of (r_{ON}) is $(r_{ON})^4 U_{i,j}[a,b]$ because the two factors of $(r_{ON})^2$ must come from diagonal entries of $\left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2}$. The other 15 terms all have at least one factor of r_{OFF}. Also, since $|r_{OFF}| < |r_{ON}|$, each of these other terms is at most $|r_{OFF}||r_{ON}|^3 \cdot \max\left(U_{i,j}\right)$. Therefore, we have

$$\left|\left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2}[a,b] - U_{i,j}[a,b]\right| \tag{E158}$$

$$\le \left|(r_{ON})^4 U_{i,j}[a,b] + 15|r_{OFF}||r_{ON}|^3 \max\left(U_{i,j}\right) - U_{i,j}[a,b]\right| \tag{E159}$$

The maximum entry in $U_{i,j}$ is $u_\alpha^{(\mathrm{Coul})}(0)$. Therefore,

$$\max\left|\left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} - U_{i,j}\right| \le u_\alpha^{(\mathrm{Coul})}(0)\left[(r_{ON})^4 - 1 + 15 \cdot |r_{OFF}| \cdot |r_{ON}|^3\right]$$

Using the bounds from Eqs. (E11) and (E12), we know that $|r_{OFF}| \le \epsilon_{i,j}(1/2 + \epsilon_{i,j}^2)$ and $|r_{ON}| \le 1 + \epsilon_{i,j}^2$. Also $\epsilon_{i,j} = \exp(\omega_{i,j}/2)$ and since by assumption $\omega_{i,j} \ge 4$, $\epsilon \le 1/4$:

$$\max\left|\left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} U_{i,j} \left(R_{i,j}^{(\mathrm{aprx})}\right)^{\otimes 2} - U_{i,j}\right| \tag{E160}$$

$$\le u_\alpha^{(\mathrm{Coul})}(0)\left[(r_{ON})^4 - 1 + 15|r_{OFF}| \cdot |r_{ON}|^3\right] \tag{E161}$$

$$\le u_\alpha^{(\mathrm{Coul})}(0)\left[(1+\epsilon_{i,j}^2)^4 - 1 + 15\epsilon_{i,j}(1/2+\epsilon_{i,j}^2)(1+\epsilon_{i,j}^2)^3\right] \tag{E162}$$

$$\le u_\alpha^{(\mathrm{Coul})}(0)\left[2\epsilon_{i,j} + 15\left(\frac{9}{16}\right)\left(\frac{17}{16}\right)^3\epsilon_{i,j}\right] \tag{E163}$$

$$\le u_\alpha^{(\mathrm{Coul})}(0)\epsilon_{i,j} \times 12 = \frac{2}{\sqrt{\pi}} 13\sqrt{\alpha}\epsilon_{i,j} \le 16\sqrt{\alpha}\epsilon_{i,j}. \tag{E164}$$

3. Proof of Lemma 9

We start with the kinetic coefficient bounds. Each $t_{(i,p),(j,q)}$ coefficient has one of the following three forms [from Eq. (C10)], depending on whether orbitals $\phi_{i,p}$ and $\phi_{j,q}$ have exponent α or β, and where x is the distance

between the two orbitals:

$$t_{\alpha,\beta}(x) = 2^{3/2}\frac{(\alpha\beta)^{7/4}}{(\alpha+\beta)^{5/2}}\left(3-2\mu x^2\right)\exp\left(-\mu x^2\right), \quad \text{where } \mu = \alpha\beta/(\alpha+\beta), \tag{E165}$$

$$t_{\alpha}(x) = \frac{\alpha}{2}\left(3-\alpha x^2\right)\exp\left(-\alpha x^2/2\right), \tag{E166}$$

$$t_{\beta}(x) = \frac{\beta}{2}\left(3-\beta x^2\right)\exp\left(-\beta x^2/2\right). \tag{E167}$$

Consider the prefactor

$$2^{3/2}\frac{(\alpha\beta)^{7/4}}{(\alpha+\beta)^{5/2}} = \frac{\sqrt{\alpha\beta}}{2}\left[\frac{\sqrt{\alpha\beta}}{\left(\frac{\alpha+\beta}{2}\right)}\right]^{5/2} \leq \frac{\sqrt{\alpha\beta}}{2}. \tag{E168}$$

The inequality follows from the fact that the geometric mean of two positive numbers is no more than their arithmetic mean. Therefore, since $\beta \geq \alpha$, the maximum prefactor for $t_\alpha(x)$, $t_\beta(x)$, or $t_{\alpha,\beta}(x)$ is

$$\max\left\{\frac{\alpha}{2}, \frac{\beta}{2}, \frac{\sqrt{\alpha\beta}}{2}\right\} = \frac{\beta}{2}. \tag{E169}$$

The part of the function t that depends on x is

$$\bar{t}_\mu(x) = (3-2\mu x^2)\exp(\mu x^2),$$

where $\mu = \alpha\beta/(\alpha+\beta)$ or $\alpha/2$ or $\beta/2$. Note that $\bar{t}_\mu(x)$ changes sign once, from positive to negative, at $2\mu x^2 = 3$. Its derivative,

$$\bar{t}'_\mu(x) = 2^{3/2}\mu x(4\mu x^2 - 10)\exp\left(-\mu x^2\right), \tag{E170}$$

vanishes only at the origin and $2\mu x^2 = 5$, where it goes from negative to positive. Therefore,

$$\max_{x\geq 0}\left|\bar{t}_\mu(x)\right| = \max\left\{\bar{t}_\mu(0), -\bar{t}_\mu(\sqrt{5/2\mu})\right\} = \bar{t}_\mu(0) = 3. \tag{E171}$$

Putting this together with the bound on the prefactor from Eq. (E169), we obtain that $t_{\max} \leq \frac{3}{2}\beta$.

$\mu \geq \alpha/2$ and therefore $2\mu\Gamma^2 \geq \alpha\Gamma^2$. Since, by assumption, $\alpha\Gamma^2 \geq 5$, we know that $\bar{t}_\mu(x)$ is monotonic for $x \geq \Gamma$. Therefore,

$$\max_{x\geq\Gamma}\left|\bar{t}_\mu(x)\right| = \left|\bar{t}_\mu(\Gamma)\right|, \tag{E172}$$

$$= \left|3-2\mu\Gamma^2\right|\exp\left(-\mu\Gamma^2\right), \tag{E173}$$

$$\leq 2\mu\Gamma^2\exp\left(-\mu\Gamma^2\right), \tag{E174}$$

$$\leq 2\exp\left(-\mu\Gamma^2/2\right) \leq 2\exp\left(-\alpha\Gamma^2/4\right), \tag{E175}$$

where in getting to the last line we use that $xe^{-x} \leq e^{-x/2}$. Putting this together with the bound on the prefactor from Eq. (E169), we obtain that $t_{\max}^{(\text{neg})} \leq \beta\exp\left(-\alpha\Gamma^2/4\right)$.

Bounding the potential integrals is easier because the integrand is strictly positive. Each potential integral corresponds to four Gaussians with centers $\mathbf{x}_1$ through $\mathbf{x}_4$ and exponents ζ_1 through ζ_4:

$$\int d\mathbf{r}d\mathbf{s}\xi_{\zeta_1}(\mathbf{r}-\mathbf{x}_1)\xi_{\zeta_2}(\mathbf{s}-\mathbf{x}_2)\frac{1}{\|\mathbf{r}-\mathbf{s}\|}\xi_{\zeta_3}(\mathbf{s}-\mathbf{x}_3)\xi_{\zeta_4}(\mathbf{r}-\mathbf{x}_4), \tag{E176}$$

$$= \prod_{i=1}^{4}\left(\frac{2\zeta_i}{\pi}\right)^{3/4}\int d\mathbf{r}d\mathbf{s}\exp\left[-\zeta_1\|\mathbf{r}-\mathbf{x}_1\|^2 - \zeta_2\|\mathbf{s}-\mathbf{x}_2\|^2 - \zeta_3\|\mathbf{s}-\mathbf{x}_3\|^2 - \zeta_4\|\mathbf{r}-\mathbf{x}_4\|^2\right]\frac{1}{\|\mathbf{r}-\mathbf{s}\|}, \tag{E177}$$

$$\leq \left(\frac{2\beta}{\pi}\right)^3\int d\mathbf{r}d\mathbf{s}\exp\left[-\alpha\left(\|\mathbf{r}-\mathbf{x}_1\|^2 + \|\mathbf{s}-\mathbf{x}_2\|^2 + \|\mathbf{s}-\mathbf{x}_3\|^2 + \|\mathbf{r}-\mathbf{x}_4\|^2\right)\right]\frac{1}{\|\mathbf{r}-\mathbf{s}\|}, \tag{E178}$$

$$= \left(\frac{2\beta}{\pi}\right)^3\int d\mathbf{r}d\mathbf{s}\exp\left[-\alpha\left(2\left\|\mathbf{r}-\frac{\mathbf{x}_1+\mathbf{x}_4}{2}\right\|^2 + \frac{1}{2}\|\mathbf{x}_1-\mathbf{x}_4\|^2 + 2\left\|\mathbf{s}-\frac{\mathbf{x}_2+\mathbf{x}_3}{2}\right\|^2 + \frac{1}{2}\|\mathbf{x}_2-\mathbf{x}_3\|^2\right)\right]\frac{1}{\|\mathbf{r}-\mathbf{s}\|}, \tag{E179}$$

$$= \left(\frac{\beta}{\alpha}\right)^3\exp\left[-\frac{\alpha}{2}\left(\|\mathbf{x}_1-\mathbf{x}_4\|^2 + \|\mathbf{x}_2-\mathbf{x}_3\|^2\right)\right]\left(\frac{2\alpha}{\pi}\right)^3\int d\mathbf{r}d\mathbf{s}$$
$$\exp\left[-\alpha\left(2\|\mathbf{r}\|^2 + 2\left\|\mathbf{s}-\frac{\mathbf{x}_2+\mathbf{x}_3-\mathbf{x}_1-\mathbf{x}_4}{2}\right\|^2\right)\right]\frac{1}{\|\mathbf{r}-\mathbf{s}\|}, \tag{E180}$$

$$= \left(\frac{\beta}{\alpha}\right)^3 \exp\left[-\frac{\alpha}{2}\left(\|\mathbf{x}_1-\mathbf{x}_4\|^2+\|\mathbf{x}_2-\mathbf{x}_3\|^2\right)\right] u_\alpha^{(\mathrm{Coul})}\left(\frac{\mathbf{x}_2+\mathbf{x}_3-\mathbf{x}_1-\mathbf{x}_4}{2}\right), \tag{E181}$$

$$\leq \beta^3\alpha^{-3}\sqrt{\frac{4\alpha}{\pi}} \leq 2\beta^3\alpha^{-5/2} \leq 2\beta^3, \tag{E182}$$

and so $u_{\max} \leq 2\beta^3$. To bound $u_{\max}^{(\mathrm{neg})}$, consider the above when at least one pair of the points $\mathbf{x}_1$ through $\mathbf{x}_4$ are at least Γ apart. If $\|\mathbf{x}_1-\mathbf{x}_4\| \geq \Gamma/2$, then the integral is at most

$$\beta^3\alpha^{-3}\exp\left[-\frac{\alpha}{2}\|\mathbf{x}_1-\mathbf{x}_4\|^2\right] u_\alpha^{(\mathrm{Coul})}(0) \leq \beta^3\alpha^{-3}\exp\left(-\alpha\Gamma^2/8\right) 2\sqrt{\alpha} \leq 2\beta^3\exp\left(-\alpha\Gamma^2/8\right) \tag{E183}$$

and similarly for $\|\mathbf{x}_2-\mathbf{x}_3\| \leq \Gamma/2$. If neither of these are the case, then at least one of $\mathbf{x}_1, \mathbf{x}_4$ must be at least Γ away from at least one of $\mathbf{x}_2, \mathbf{x}_3$. Without loss of generality, suppose that $\|\mathbf{x}_1-\mathbf{x}_2\| \geq \Gamma$. That $\|\mathbf{x}_1-\mathbf{x}_4\| \leq \Gamma/2$ implies

$$\left\|\frac{\mathbf{x}_1+\mathbf{x}_4}{2}-\mathbf{x}_1\right\| \leq \frac{\Gamma}{4} \tag{E184}$$

and similarly for $\mathbf{x}_2$ and $\mathbf{x}_3$. Then,

$$\left\|\frac{\mathbf{x}_2+\mathbf{x}_3-\mathbf{x}_1-\mathbf{x}_4}{2}\right\| = \left\|\left(\underbrace{\frac{\mathbf{x}_2+\mathbf{x}_3}{2}-\mathbf{x}_2}_{\leq\Gamma/4}\right)-\left(\underbrace{\frac{\mathbf{x}_1+\mathbf{x}_4}{2}-\mathbf{x}_1}_{\leq\Gamma/4}\right)+\left(\underbrace{\mathbf{x}_2-\mathbf{x}_1}_{\geq\Gamma}\right)\right\| \geq \Gamma-\frac{\Gamma}{4}-\frac{\Gamma}{4}=\frac{\Gamma}{2} \tag{E185}$$

and the potential integral is at most

$$\beta^3 u_\alpha^{(\mathrm{Coul})}(\Gamma/2) = \beta^3\sqrt{\frac{4\alpha}{\pi}}F_0(\alpha\Gamma^2/4) \leq \beta^3\sqrt{\frac{4\alpha}{\pi}}\sqrt{\frac{\pi}{4}}\frac{1}{\sqrt{\alpha\Gamma^2/4}} = 2\beta^3\frac{1}{\Gamma}. \tag{E186}$$

Together with Eq. (E182), this yields

$$u_{\max}^{(\mathrm{neg})} \leq \max\left\{2\beta^3\exp(-\alpha\Gamma^2/8), 2\beta^3\Gamma^{-1}\right\} = 2\beta^3\max\{\exp(-\alpha\Gamma^2/8), \Gamma^{-1}\}. \tag{E187}$$

For $\alpha\Gamma^2 \geq 64$ (a condition of the lemma),

$$\frac{1}{\exp(-\alpha\Gamma^2/8)} = \exp(\alpha\Gamma^2/8) = \sum_{k=0}^{\infty}\frac{1}{k!}\left(\frac{\alpha}{8}\Gamma^2\right)^k \tag{E188}$$

$$\leq \frac{\alpha}{8}\Gamma^2 \leq \frac{\alpha^2}{8}\Gamma^2 = \sqrt{\frac{\alpha\Gamma^2}{64}}\Gamma \geq \Gamma \tag{E189}$$

and so

$$u_{\max}^{(\mathrm{neg})} \leq 2\beta^3/\Gamma. \tag{E190}$$

■

APPENDIX F: HARDNESS OF FINDING LOWEST-ENERGY SLATER DETERMINANT

In this appendix, we show that finding the lowest-energy Slater determinant (i.e., the Hartree-Fock state) of an electronic-structure Hamiltonian is NP hard. This is a natural complement to our QMA-hardness result, in that Slater determinants are the most natural class of fermionic states that are efficiently representable and manipulable classically. The proof has much in common with that of Theorem 1. We start with the same parametrized construction of orbitals described in Sec. C 1 and then orthonormalize and round them as in Sec. C 2 to obtain the Hamiltonian $H^{(\mathrm{round})}$. We then diverge from the QMA-hardness proof by setting the parameters in a different regime. Specifically, we set the exponents α and β large enough that the Hamiltonian becomes essentially classical (diagonal). The proof concludes by showing that this classical Hamiltonian can express an NP-hard problem such as independent set.

Theorem 3: *Determining the lowest-energy Slater determinant of an electronic-structure Hamiltonian in a fixed basis and with a fixed particle number to inverse-polynomial precision is NP-complete.*

Proof. To start, we set $\gamma_{i,j} = \gamma$ for all $\{i,j\} \in E$. We show that the parameters α, β, γ, Γ can be set such that the

electronic structure approximates a diagonal Hamiltonian

$$H^{(\mathrm{ES})} - n \cdot c_T \approx H^{(\mathrm{class})} = u_1^{(\mathrm{class})} \sum_i n_{i,+1} n_{i,-1} + u_2^{(\mathrm{class})} \sum_{\substack{\{i,j\}\in E \\ \sigma,\tau\in\{\pm 1\}}} n_{i,\sigma} n_{j,\tau}, \quad \text{(F1)}$$

where

$$u_1^{(\mathrm{class})} = c_U^{(\mathrm{round})}, \quad u_2^{(\mathrm{class})} = \frac{1}{4d^2} u_\alpha^{(\mathrm{Coul})}(\gamma). \quad \text{(F2)}$$

For a diagonal Hamiltonian, there is always a computational basis state of lowest energy. Because basis states are a special case of Slater determinants, finding the lowest-energy Slater determinant for diagonal Hamiltonians is equivalent to finding the ground state.

For sufficiently large $u_1^{(\mathrm{class})} > 4n^2 u_2^{(\mathrm{class})}$, the ground space of $H^{(\mathrm{class})}$ in the k-electron subspace for $k \le n$ has at most one electron in each spatial orbital and the ground-state energy is

$$h(\mathbf{n}) = u_2^{(\mathrm{class})} \sum_{\{i,j\}\in E} n_i n_j, \quad \text{(F3)}$$

where $n_i = n_{i,+1} + n_{i,-1}$ is the occupancy of the ith spatial orbital.

The state space is spanned by vectors $\mathbf{n}$ such that $\sum_i n_i = k$, which we can interpret as representing a subset $S \subset V$ of vertices with size $|S| = k$. The classical function $h(\mathbf{n})$ is then proportional to the number of edges with both endpoints in the set S. In other words, if $h(\mathbf{n}) = 0$, then the set S is an independent set of size k; otherwise, $h(\mathbf{n}) \ge u_2^{(\mathrm{class})}$. Therefore, if $u_1^{(\mathrm{class})}$ is sufficiently larger than $u_2^{(\mathrm{class})}$, then finding the lowest-energy Slater determinant of $H^{(\mathrm{class})}$ in the k-electron subspace to precision $u_2^{(\mathrm{class})}$ is as hard as determining if a graph has an independent set of size k.

To finish the proof, we just need to set the parameters such that

$$u_1^{(\mathrm{class})} > 4n^2 u_2^{(\mathrm{class})}, \quad \text{(F4)}$$

$$\left\| H^{(\mathrm{ES})} - H^{(\mathrm{class})} \right\| < \frac{1}{2} u_2^{(\mathrm{class})}. \quad \text{(F5)}$$

Let $\gamma = 1$, leaving α, β, and Γ to be set. The first constraint is satisfied by $\beta \ge 16n^4$:

$$u_1^{(\mathrm{class})} = c_U^{(\mathrm{round})} \ge \frac{1}{4} u_\beta^{(\mathrm{Coul})}(0) \quad \text{(F6)}$$

$$= \frac{1}{4}\sqrt{\frac{4\beta}{\pi}} > \frac{1}{4}\sqrt{\beta} \quad \text{(F7)}$$

$$\ge n^2 \quad \text{(F8)}$$

$$\ge \frac{n^2}{d^2} \operatorname{erf}\left(\sqrt{\alpha\gamma^2}\right) \quad \text{(F9)}$$

$$= 4n^2 u_2^{(\mathrm{class})}. \quad \text{(F10)}$$

For the second constraint, if $\alpha \ge 1$, then

$$\frac{1}{2} u_2^{(\mathrm{class})} \ge \frac{1}{2}\frac{1}{4d^2} \operatorname{erf} 1 \ge \frac{1}{8n^2}\frac{1}{2} \ge \frac{1}{16n^2}. \quad \text{(F11)}$$

Lemma 10: *For $\alpha \ge 1$, $\gamma_{i,j} = \gamma \ge 1$,*

$$\left\| H^{(round)} - H^{(class)} \right\| \le 14\alpha n^2 e^{-\alpha\gamma^2/4}. \quad \text{(F12)}$$

Proof of Lemma 10. The classical Hamiltonian $H^{(\mathrm{class})}$ has no kinetic component and so we need to bound the entirety of the nonconstant kinetic component of the rounded Hamiltonian $H^{(\mathrm{round})}$:

$$\left\| T^{(\mathrm{round})} - n \cdot c_T \right\| = \left\| \sum_{\substack{\{i,j\}\in E \\ \sigma\in\{\pm 1\}}} t_{i,j}^{(\mathrm{round})} \right\| \left(a_{i,\sigma}^\dagger a_{j,\sigma} + a_{j,\sigma}^\dagger a_{i,\sigma} \right) \quad \text{(F13)}$$

$$\le 4 \sum_{\{i,j\}\in E} \left| t_{i,j}^{(\mathrm{round})} \right| \quad \text{(F14)}$$

$$\le \frac{\alpha}{d} n^2 \sqrt{f(\omega)} \le \alpha^2 n^2 \gamma^2 e^{-\alpha\gamma^2/2}. \quad \text{(F15)}$$

For the potential difference, define

$$B_3 = B_2 \setminus \{(i,j,j,i) : \{i,j\} \in E\}, \quad \text{(F16)}$$

i.e., the indices of potential terms that are *not* Coulomb (which are exactly those included in $H^{(\mathrm{class})}$). Then,

$$\left\| U^{(\text{round})} - H^{(\text{class})} \right\| \tag{F17}$$

$$= \left\| \frac{1}{2} \sum_{\substack{(i,j,k,l)\in B \\ \sigma,\tau\in\{\pm 1\}}} u^{(\text{round})}_{i,j,k,l} a^\dagger_{i,\sigma} a^\dagger_{j,\tau} a_{k,\tau} a_{l,\sigma} - u^{(\text{class})}_1 \sum_{i\in[n]} n_{i,+1} n_{i,-1} - u^{(\text{class})}_2 \sum_{\substack{\{i,j\}\in E \\ \sigma,\tau\in\{\pm 1\}}} n_{i,\sigma} n_{j,\tau}, \right\| \tag{F18}$$

$$\leq \frac{1}{2} \sum_{\substack{(i,j,k,l)\in B_3 \\ \sigma,\tau\in\{\pm 1\}}} u^{(\text{round})}_{i,j,k,l} \tag{F19}$$

$$\leq \frac{1}{2} \times \underbrace{4}_{\sigma,\tau} \times \underbrace{12 \times \binom{n}{2}}_{B_3} \times \frac{1}{4d^2} 2\sqrt{\alpha} \exp\left(-\alpha\gamma^2/2\right) \tag{F20}$$

$$\leq 6\sqrt{\alpha} n^2 \exp\left(-\alpha\gamma^2/2\right). \tag{F21}$$

Putting them together,

$$\left\| H^{(\text{round})} - H^{(\text{class})} \right\| \leq \left\| T^{(\text{round})} - n \cdot c_T \right\| + \left\| U^{(\text{round})} - H^{(\text{class})} - n \cdot c_T \right\|, \tag{F22}$$

$$\leq 7\alpha n^2 (\alpha\gamma^2) e^{-\alpha\gamma^2/2} \leq 14\alpha n^2 e^{-\alpha\gamma^2/4}. \tag{F23}$$

■

Together, Lemmas 1 and 10 imply that for $\gamma = 1$, $\beta \geq \alpha > 74 + 48\log n$, $\Gamma \geq 640 n^{18}\beta^3$, and $\alpha\Gamma^2 \geq 12\log\beta + 80\log n + 4\alpha + 24$,

$$\left\| H^{(\text{ES})} - H^{(\text{class})} - n \cdot c_T \right\| \leq \left\| H^{(\text{ES})} - H^{(\text{round})} \right\| + \left\| H^{(\text{round})} - H^{(\text{class})} - n \cdot c_T \right\| \tag{F24}$$

$$\leq 3n^2\alpha f\left(\omega_{\min}\right) + \frac{1}{20n^2} + 8n^4\sqrt{\alpha}\exp(-\omega_{\min}/2) + 14\alpha n^2 e^{-\alpha\gamma^2/4} \tag{F25}$$

$$= 3n^2\alpha^2 e^{-\alpha/2} + \frac{1}{20n^2} + 8n^4\sqrt{\alpha}\exp(-\alpha/2) + 14\alpha n^2 e^{-\alpha/4} \tag{F26}$$

$$\leq \frac{1}{20n^2} + 100 n^4 e^{-\alpha/8} \leq \frac{1}{20n^2} + \frac{1}{80n^2} = \frac{1}{16n^2}, \tag{F27}$$

where use the fact that for $x \geq 0$, $\max\{x^2 e^{-x/2}, \sqrt{x} e^{-x/2}, x e^{-x/4}\} \leq 4e^{-x/8}$. For sufficiently large n, it suffices to set $\beta = \alpha = n$, $\gamma = 1$ and $\Gamma = n^{32}$. ■

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