The effect of quantization on the FCIQMC sign problem

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The sign problem in Full Configuration Interaction Quantum Monte Carlo (FCIQMC) without annihilation can be understood as an instability of the psi-particle population to the ground state of the matrix obtained by making all off-diagonal elements of the Hamiltonian negative. Such a matrix, and hence the sign problem, is basis dependent. In this paper we discuss the properties of a physically important basis choice: first versus second quantization. For a given choice of single-particle orbitals, we identify the conditions under which the fermion sign problem in the second quantized basis of antisymmetric Slater determinants is identical to the sign problem in the first quantized basis of unsymmetrized Hartree products. We also show that, when the two differ, the fermion sign problem is always less severe in the second quantized basis. This supports the idea that FCIQMC, even in the absence of annihilation, improves the sign problem relative to first quantized methods. Finally, we point out some theoretically interesting classes of Hamiltonians where first and second quantized sign problems differ, and others where they do not.

I. INTRODUCTION

Projector quantum Monte Carlo methods such as Diffusion Quantum Monte Carlo[1] (DMC) and Full Configuration Interaction Quantum Monte Carlo[2] (FCIQMC) generate a stochastic representation of the solution of the imaginary-time Schrödinger equation, $\partial|\psi\rangle/\partial\tau = -\widehat{H}|\psi\rangle$. As long as the starting state $|\psi(\tau=0)\rangle$ has a non-zero overlap with the ground state $|\psi_0\rangle$, the solution $|\psi(\tau)\rangle$ converges to $|\psi_0\rangle$ as $\tau\to\infty$, up to a normalization. In FCIQMC, the Hamiltonian is represented in a finite discrete basis, typically Slater determinants. The imaginary-time Schrödinger equation is thus expressed in the matrix formulation,

$$\frac{dc_{\mathbf{i}}(\tau)}{d\tau} = -\sum_{\mathbf{j}}\langle\mathbf{i}|\left(\widehat{H}-S\widehat{I}\right)|\mathbf{j}\rangle c_{\mathbf{j}}(\tau), \qquad (1)$$

where $|\mathbf{i}\rangle$ represents a many-particle basis function (e.g. a determinant), $c_{\mathbf{i}}(\tau)=\langle\mathbf{i}|\psi(\tau)\rangle$ is the component of $|\psi(\tau)\rangle$ along $|\mathbf{i}\rangle$, S is a parameter which can be adjusted to control the normalization, and $\widehat{I}$ is the identity operator. We define $H_{\mathbf{ij}}\equiv\langle\mathbf{i}|(\widehat{H}-S\widehat{I})|\mathbf{j}\rangle$ and assume that $\widehat{H}$ has time-reversal symmetry, so that $H_{\mathbf{ij}}$ and thus $c_{\mathbf{i}}(\tau)$ can be chosen to be real.

In FCIQMC, an initial population of signed *psi-particles* or *psips* (not to be confused with the real particles of the system) is distributed over the Hilbert space such that the expected value of the signed psip population on $|\mathbf{i}\rangle$ is proportional to $c_{\mathbf{i}}(0)$. The psip distribution is then evolved in time using an algorithm which ensures that the expected value of the signed population on $|\mathbf{i}\rangle$ remains proportional to $c_{\mathbf{i}}(\tau)$. In the $\tau\to\infty$ limit, the psip distribution provides a stochastic snapshot of the ground state wave function.[1–3]

The amplitudes $c_{\mathbf{i}}(\tau)$ and $c_{\mathbf{i}}(\tau+\Delta\tau)$ of a solution to Eq. (1) are related by the formula

$$c_{\mathbf{i}}(\tau+\Delta\tau) = \sum_{\mathbf{j}}\langle\mathbf{i}|e^{-(\widehat{H}-S\widehat{I})\Delta\tau}|\mathbf{j}\rangle c_{\mathbf{j}}(\tau), \qquad (2)$$

for which different projector QMC methods use different approximations for the exponential. For instance, DMC in the continuum uses a Trotter approximation to generate the transition matrix $\mathbf{U}_{\mathrm{DMC}}(\mathbf{R},\mathbf{R}')\equiv\langle\mathbf{R}|e^{-\widehat{T}\Delta\tau}e^{-(\widehat{V}-S\widehat{I})\Delta\tau}|\mathbf{R}'\rangle$, where $\widehat{T}$ and $\widehat{V}$ are the kinetic and potential energy operators, and $\mathbf{R}$ and $\mathbf{R}'$ are positions in the $3N$-dimensional space of particle coordinates. In FCIQMC, a first-order finite difference approximation is used instead: $e^{-\mathbf{H}\Delta\tau}\approx\mathbf{I}-\mathbf{H}\Delta\tau\equiv\mathbf{U}_{\mathrm{FCIQMC}}$. If the product of the time step $\Delta\tau$ and the largest eigenvalue $E_{\max}$ of H is not too large, then the ground state of $\mathbf{H}$ is the same as the *dominant* eigenvector of $\mathbf{U}_{\mathrm{FCIQMC}}$. Note that throughout this paper we use the term 'dominant' to mean the eigenvector with the largest eigenvalue. Similarly, in Lattice Regularized DMC (LRDMC), where an upper bound on $\widehat{H}$ is introduced by adding an artificial lattice[4], one also uses the transition matrix $\mathbf{U}_{\mathrm{LRDMC}}=\mathbf{I}-\mathbf{H}\Delta\tau$. In this paper, we focus primarily on the case of FCIQMC. However, by formulating our arguments in terms of the transition matrix $\mathbf{U}$, most of our results are applicable to all projector QMC methods.

II. GENERAL PROPERTIES OF THE SIGN PROBLEM

FCIQMC is a stochastic algorithm for applying the real symmetric matrix $\mathbf{U}_{\mathrm{FCIQMC}}$ (which we call $\mathbf{U}$ from now on) to a population of psips. Because FCIQMC works

in a discrete basis, two psips of opposite sign occasionally end up on the same basis function, at which point they cancel out and can be removed from the simulation. When FCIQMC was initially proposed, it was observed that this process, known as 'annihilation,' is critical in order for the psip distribution to converge to the ground state[2]. Two of us subsequently showed[3] that:

1. In the absence of annihilation, the densities of positive ($\{c_{\mathbf{i}}^+\}$) and negative ($\{c_{\mathbf{i}}^-\}$) psips evolve according to coupled equations. The out-of-phase component, $c_{\mathbf{i}}^+ - c_{\mathbf{i}}^-$, evolves according to

$$c_{\mathbf{i}}^+(\tau+\Delta\tau) - c_{\mathbf{i}}^-(\tau+\Delta\tau) = \sum_{\mathbf{j}} U_{\mathbf{ij}} \left[c_{\mathbf{i}}^+(\tau) - c_{\mathbf{i}}^-(\tau)\right] \quad (3)$$

   and converges to the dominant eigenstate of $\mathbf{U}$, i.e., the ground state of $\mathbf{H}$. In contrast, the evolution of the in-phase component, $c_{\mathbf{i}}^+ + c_{\mathbf{i}}^-$, is governed by a different matrix $\widetilde{\mathbf{U}}$, the elements of which are the absolute values of the elements of $\mathbf{U}$:

$$\widetilde{U}_{\mathbf{ij}} = \left|U_{\mathbf{ij}}\right| . \quad (4)$$

2. The largest eigenvalue of $\widetilde{\mathbf{U}}$ is *always* greater than or equal to the largest eigenvalue of $\mathbf{U}$. Thus, in the absence of annihilation, both $c_{\mathbf{i}}^+$ and $c_{\mathbf{i}}^-$ tend to the dominant eigenvector of $\widetilde{\mathbf{U}}$. The physical ground state can in principle be obtained by subtracting $c_{\mathbf{i}}^-$ from $c_{\mathbf{i}}^+$, but the difference is exponentially smaller than $c_{\mathbf{i}}^+$ and $c_{\mathbf{i}}^-$. In a real simulation using a finite number of psips, the difference is swamped by the statistical noise in $c_{\mathbf{i}}^+$ and $c_{\mathbf{i}}^-$; this is the sign problem in the FCIQMC method. The severity of the sign problem depends on the difference between the largest eigenvalues of $\mathbf{U}$ and $\widetilde{\mathbf{U}}$.

For projector methods such as FCIQMC and LRDMC, which are based on a transition matrix of the form $\mathbf{U} \equiv \mathbf{I} - \mathbf{H}\Delta\tau$, we can talk instead about the properties of $\widetilde{\mathbf{H}}$, the matrix obtained by making all off-diagonal elements of $\mathbf{H}$ negative:

$$\widetilde{H}_{\mathbf{ij}} = -\left|H_{\mathbf{ij}}\right| ; \quad \widetilde{H}_{\mathbf{ii}} = H_{\mathbf{ii}} . \quad (5)$$

Since the diagonal elements of $\mathbf{U}$ are always positive for small enough $\Delta\tau$, the diagonals of $\widetilde{\mathbf{U}}$ and $\mathbf{U}$ match. By construction, so do the diagonals of $\widetilde{\mathbf{H}}$ and $\mathbf{H}$. Thus, for small enough $\Delta\tau$, $\widetilde{\mathbf{U}} = \mathbf{I} - \widetilde{\mathbf{H}}\Delta\tau$, so the ground state of $\widetilde{\mathbf{H}}$ is identical to the dominant eigenstate of $\widetilde{\mathbf{U}}$.

III. COMPARISON OF FIRST AND SECOND QUANTIZED SIGN PROBLEMS

The analysis of the sign problem in Ref. 3 did not assume anything about the choice of basis, and in particular did not require that the basis be first quantized (unsymmetrized, as in DMC simulations[1,4,5]) or second quantized (symmetrized or antisymmetrized, as in FCIQMC simulations of bosonic or fermionic systems, respectively[2]). In this paper, we compare the sign problems for many-fermion systems expressed in first and second quantized bases, answering two questions. First, when are the sign problems of first and second quantized algorithms different? Second, when they differ, which is better?

In order to be clear about the basis in which a quantity is expressed, we shall use the subscripts F, D and P to indicate a first quantized basis of Hartree products, a second quantized basis of Slater determinants, and a second quantized basis of permanents, respectively. A quantity without any subscript is general and can be considered in any of the three bases.

Let us consider a basis of Hartree products, $\{|\mathbf{i}\rangle\}$, for a system of N fermions and M mutually orthogonal single-particle basis functions, where $|\mathbf{i}\rangle = |\phi_{i_1}(1)\phi_{i_2}(2)\cdots\phi_{i_N}(N)\rangle$ and multiple occupancy of any single-particle basis function, ϕ_j, is forbidden. The vector index $\mathbf{i}$ defines the list of N single-particle basis functions appearing in a Hartree product and specifies the order in which those basis functions occur. The first quantized Hamiltonian is formed by taking matrix elements of the Hamiltonian operator with respect to the ${}^M P_N$ Hartree products, so that each eigenstate of the Hamiltonian can be written as a linear combination of the form $|\psi\rangle = \sum_{\mathbf{i}} c_{\mathbf{i}}|\mathbf{i}\rangle$. However, physically meaningful many-fermion wave functions must be totally antisymmetric with respect to exchange of any two fermions and hence may also be expressed as linear combinations of Slater determinants.

The fermionic second quantized basis is thus the set of ${}^M C_N$ determinants $\{|D_{\mathbf{i}}\rangle\}$. We use the notation $|\mathbf{i}\rangle \in |D_{\mathbf{i}}\rangle$ to indicate that the Hartree product $|\mathbf{i}\rangle$ is a permutation of the orbitals in $|D_{\mathbf{i}}\rangle$. For $|\mathbf{i}\rangle \in |D_{\mathbf{i}}\rangle$, $|D_{\mathbf{i}}\rangle$ can be obtained from $|\mathbf{i}\rangle$ using the antisymmetrization operator $\mathcal{A}$, defined by

$$\mathcal{A}|\phi_{i_1}(1)\phi_{i_2}(2)\cdots\phi_{i_N}(N)\rangle = \frac{1}{N!}\sum_P (-1)^{\zeta_P}|\phi_{i_{P(1)}}(1)\cdots\phi_{i_{P(N)}}(N)\rangle , \quad (6)$$

where P labels permutations of the N orbitals and ζ_P is the sign of the permutation. Then $\mathcal{A}|\mathbf{i}\rangle = \frac{\mathrm{sgn}\langle\mathbf{i}|D_{\mathbf{i}}\rangle}{\sqrt{N!}}|D_{\mathbf{i}}\rangle$, where the factor of $\sqrt{N!}$ ensures that $|\mathbf{i}\rangle$ and $|D_{\mathbf{i}}\rangle$ remain normalized. The order of the orbitals appearing in a determinant $|D_{\mathbf{i}}\rangle = (N!)^{1/2}\mathcal{A}|\phi_{i_1}(1)\phi_{i_2}(2)\cdots\phi_{i_N}(N)\rangle$ affects only the overall sign. Hence, to uniquely specify each determinant, we insist that $i_1 < i_2 < \cdots < i_N$. We utilize a similar notation for the (bosonic) basis of permanents, $\{|P_{\mathbf{i}}\rangle\}$, defined by $|P_{\mathbf{i}}\rangle = \sqrt{N!}\,\mathcal{S}|\mathbf{i}\rangle$, where $\mathcal{S}$ is the symmetrizer. Throughout this paper, we exploit the fact that there is a one-to-one mapping between $|D_{\mathbf{i}}\rangle$ and $|P_{\mathbf{i}}\rangle$, which holds because the single-particle orbitals are orthogonal and multiple occupancy of any given single-particle orbital is forbidden. In the context of the bosonic

permanents, this corresponds to an effective hardcore constraint in the space of single-particle orbitals.

To get a feel for how the sign problem could be worse in a first quantized formalism than in second quantized one, consider a first quantized psip on $|\mathbf{i}\rangle$ that is connected by off-diagonal elements of $\widehat{U}$ to $|\mathbf{j}\rangle$ and $|\mathbf{j}'\rangle$. If the orbitals in $\mathbf{j}$ and $\mathbf{j}'$ are permutations of one another, then $|\mathbf{j}\rangle$ and $|\mathbf{j}'\rangle$ both appear in the expansion of the same determinant: $|\mathbf{j}\rangle, |\mathbf{j}'\rangle \in |D_\mathbf{j}\rangle$. After a single step of the FCIQMC algorithm, it is possible for the antisymmetrizer to map these two psips to $|D_\mathbf{j}\rangle$ with opposite signs, as illustrated in Fig. 1. If the amplitude of $|\psi(\tau)\rangle$ on $|D_\mathbf{j}\rangle$ is small, the cancellation of the two first quantized contributions needs to be very accurate to stochastically obtain the correct amplitude. In practice, the small signal is swamped by statistical fluctuations in the first quantized psip populations and a sign problem results. FCIQMC in a determinant basis performs this cancellation automatically. Therefore, as we rigorously prove in Appendix A, the first and second quantized sign problems are identical if and only if the two first quantized psips always contribute with the same sign to the total weight on $|D_\mathbf{j}\rangle$. This argument also suggests that, if the sign problems differ, the second quantized algorithm will be better.

To define the difference between sign problems more explicitly, we consider the ground state properties of $\widetilde{\mathbf{U}}$ in a first and second quantized basis. In the first quantized basis, both $\mathbf{U}_F$ and $\widetilde{\mathbf{U}}_F$ commute with arbitrary permutations of the particle labels. Therefore, the dominant eigenstate $|\widetilde{\varphi}_F\rangle$ of $\widetilde{\mathbf{U}}_F$ must transform according to an irreducible representation of the permutation group. Since all elements of $\widetilde{\mathbf{U}}_F$ are non-negative in the $|\mathbf{i}\rangle$ basis, it may be shown via a simple variational argument that all non-zero components $\langle\mathbf{i}|\widetilde{\varphi}_F\rangle$ have the same sign, and hence that $|\widetilde{\varphi}_F\rangle$ has a non-zero overlap with the bosonic state $|\psi_B\rangle = \sum_\mathbf{i} |\mathbf{i}\rangle$. As eigenvectors transforming according to different irreducible representations are orthogonal, it follows that $|\widetilde{\varphi}_F\rangle$ must also be a bosonic state. Therefore, $|\widetilde{\varphi}_F\rangle$ may equally well be regarded as the dominant eigenvector of the matrix $\langle P_\mathbf{i}|\widetilde{\mathbf{U}}_F|P_\mathbf{j}\rangle$ obtained by evaluating the matrix elements of $\widetilde{\mathbf{U}}_F$ in the basis of permanents.

Meanwhile, the second quantized algorithm is unstable with respect to the dominant eigenstate of the matrix $\widetilde{\mathbf{U}}_D$ with elements $|\langle D_\mathbf{i}|\mathbf{U}_F|D_\mathbf{j}\rangle|$. Although the matrices $\langle P_\mathbf{i}|\widetilde{\mathbf{U}}_F|P_\mathbf{j}\rangle$ and $\widetilde{\mathbf{U}}_D$ have the same size – each containing $(N!)^2$ fewer elements than $\widetilde{\mathbf{U}}_F$ in a Hartree product basis – they are not in general the same matrix. Whenever they differ, we prove in Appendix A that the dominant eigenvalue of $\widetilde{\mathbf{U}}_D$ is smaller than the dominant eigenvalue of $\langle P_i|\widetilde{\mathbf{U}}_F|P_j\rangle$; the second quantized sign problem is therefore less severe than the first quantized sign problem. The sign problems in the first and second quantized bases are the same if and only if the two matrices are the same:

$$\langle P_\mathbf{i}|\widetilde{\mathbf{U}}_F|P_\mathbf{j}\rangle = \langle D_\mathbf{i}|\widetilde{\mathbf{U}}_D|D_\mathbf{j}\rangle. \tag{7}$$

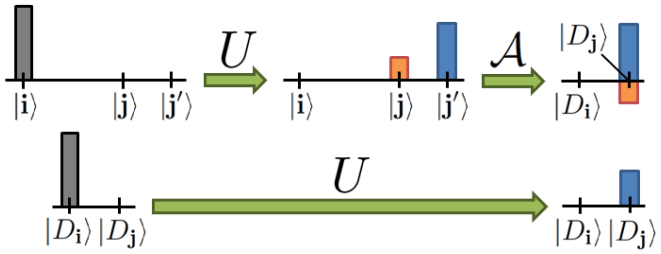

FIG. 1. A single step of the FCIQMC algorithm, illustrating how the first and second quantized sign problems can differ. (Top) In the first quantized algorithm, a psip on $|\mathbf{i}\rangle$ may spawn children on two different Hartree products, $|\mathbf{j}\rangle$ and $|\mathbf{j}'\rangle$, belonging to the same determinant: $|\mathbf{j}\rangle, |\mathbf{j}'\rangle \in |D_\mathbf{j}\rangle$. After antisymmetrizing, the psips may contribute with opposite sign to the total weight on $|D_\mathbf{j}\rangle$. (Bottom) Performing the same step in the second quantized algorithm, the cancellation on $|D_\mathbf{j}\rangle$ is automatically accounted for by the sign and magnitude of $\langle D_\mathbf{i}|\widehat{U}|D_\mathbf{j}\rangle$.

In the Appendix, we also prove that this condition is equivalent to our previous conditions on the psip dynamics, as discussed above and illustrated in Fig. 1.

It is worth noting that in FCIQMC and LRDMC, where $\widetilde{\mathbf{U}}_F = \mathbf{I} - \widetilde{\mathbf{H}}_F\Delta\tau$, $|\widetilde{\varphi}_F\rangle$ is also the bosonic ground state of $\widetilde{\mathbf{H}}_F$. This state is not in general the same as the physical many-boson ground state, which is the lowest-energy totally-symmetric eigenstate of $\mathbf{H}_F$. For LRDMC in real space, however, all off-diagonal elements of $\mathbf{U}_F$ are already positive, so $\mathbf{U}_F = \widetilde{\mathbf{U}}_F$, $\mathbf{H}_F = \widetilde{\mathbf{H}}_F$, and the instability *is* with respect to the physical bosonic ground state for this special case.

IV. EXAMPLES FOR PHYSICAL HAMILTONIANS

There are a number of physical situations in which the equivalence condition, Eq. (7), holds. The simplest is when the two-particle part of the Hamiltonian operator is diagonal in the Hartree product basis, so that all off-diagonal matrix elements are single-particle in nature. Important such physical examples are the Hubbard model in real space and the LRDMC algorithm. For these Hamiltonians, the psips accumulate a (diagonal) weight according to the electronic potential and move (off-diagonally) according to the one-body kinetic operator. To illustrate the relationship between first and second quantized psip populations in such a system, Fig. 2 plots their distributions for a simple problem involving two spinless fermions hopping between nearest-neighbor sites on a two-dimensional square lattice. As expected, the first and second quantized psip distributions are step-by-step identical, after antisymmetrization.

A more general case where the sign problems are equivalent is when, in the space of determinants, all exchange integrals in diagonal matrix elements are non-negative and all off-diagonal matrix elements involve only a sin-

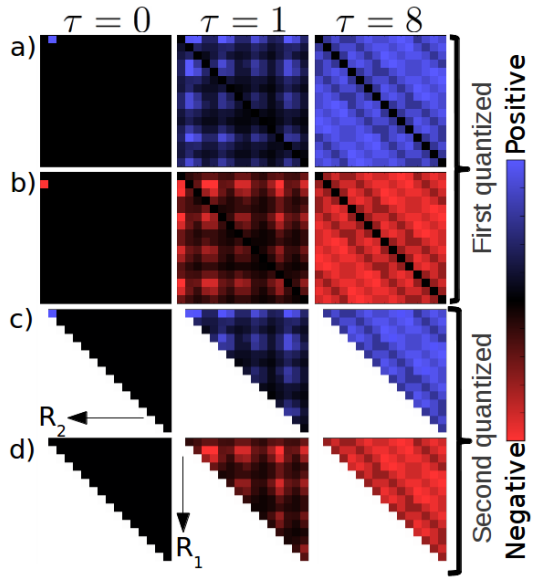

FIG. 2. Comparison of first and second quantized psip distributions for an FCIQMC simulation of two spinless fermions interacting via the Hamiltonian $\widehat{H} = -\sum_{\langle ij\rangle}\left[c_i^\dagger c_j + c_j^\dagger c_i - n_i n_j\right]$, where the sum is over nearest neighbors of a 4×4 square lattice with periodic boundary conditions. Images show the probability distributions of positive (a,c) and negative (b,d) psips separately as functions of the imaginary time τ. The propagation is performed analytically according to Eq. (2) using the approximation $\mathbf{U}_{\text{FCIQMC}} = \mathbf{I} - \mathbf{H}\Delta\tau$ with time step $\Delta\tau = 0.1$. While the positive and negative psip populations individually converge to the ground state of $\widetilde{\mathbf{H}}$ ($E = -7.41589748$), their exponentially small difference (not shown) converges to the ground state of $\mathbf{H}$ ($E = -5.89171753$).[6] Note that the upper right-hand triangles of comparable distributions (positive first quantized and positive second quantized, for example) match. The "missing" triangles can be reconstructed by expanding out the Slater determinants, after which the psip distributions are step-by-step identical. A psip located at (R_i, R_j) represents the Hartree product $|\phi_i(1)\phi_j(2)\rangle$ or Slater determinant $\sqrt{2}\mathcal{A}|\phi_i(1)\phi_j(2)\rangle$, where ϕ_i is a single-particle basis function at the lattice vertex (x_i, y_i) and $R_i = x_i + 4y_i$.

gle integral. To understand these conditions, consider an arbitrary Hamiltonian with one-particle interaction $\hat{h}$ and two-particle interaction $\hat{u}_{12}$. If only one off-diagonal integral is non-zero, then off-diagonal elements on both sides of Eq. (7) are just the negative absolute value of the non-zero term[7]. Similarly, the restriction on diagonal exchange integrals is necessary to make the diagonal elements of Eq. (7) match. As exchange terms occur only in the off-diagonal elements of the first quantized Hamiltonian $\mathbf{H}_F$, they enter $\langle P|\widetilde{\mathbf{H}}_F|P\rangle$ with negative magnitude by the definition of $\widetilde{\mathbf{H}}_F$:

$$\begin{aligned}\langle P|\widetilde{\mathbf{H}}_F|P\rangle =& \frac{1}{N!}\sum_{\mathbf{i}\in P}\langle \mathbf{i}|H_F|\mathbf{i}\rangle + \frac{1}{N!}\sum_{\mathbf{i}\in P}\sum_{\substack{\mathbf{j}\in P\\ \mathbf{j}\neq\mathbf{i}}}\Big[-\big|\langle \mathbf{i}|H_F|\mathbf{j}\rangle\big|\Big]\\ =& \sum_i \langle i|\hat{h}|i\rangle + \sum_{i<j}\langle ij|\hat{u}_{12}|ij\rangle - \sum_{i<j}\big|\langle ij|\hat{u}_{12}|ji\rangle\big|\ ,\end{aligned} \tag{8}$$

where $\phi_{i,j}$ are single-particle basis functions occupied in D and P. Meanwhile, $\langle D|\widetilde{\mathbf{H}}_D|D\rangle$ is simply the matrix element of the second quantized Hamiltonian:

$$\begin{aligned}\langle D|\widetilde{\mathbf{H}}_D|D\rangle =& \langle D|\mathbf{H}_D|D\rangle\\ =& \sum_i \langle i|\hat{h}|i\rangle + \sum_{i<j}\langle ij|\hat{u}_{12}|ij\rangle - \sum_{i<j}\langle ij|\hat{u}_{12}|ji\rangle\ .\end{aligned} \tag{9}$$

Clearly Eqs. (8) and (9) match if and only if the diagonal exchange integrals are positive.

The Hubbard model in momentum space is an example where these conditions are met: First, there are no exchange contributions to the diagonal Hamiltonian matrix elements. Second, every member $|\mathbf{j}\rangle$ of the set $\{|\mathbf{j}\rangle\}$ of Hartree products obtained by applying the momentum-space Hubbard Hamiltonian to an arbitrary Hartree product $|\mathbf{i}\rangle$ differs from $|\mathbf{i}\rangle$ by at most one spin-up orbital and one spin-down orbital. As no two such Hartree products in $\{|\mathbf{j}\rangle\}$ can contain the same set of occupied orbitals, no two Hartree products in $\{|\mathbf{j}\rangle\}$ can appear in the expansion of the same determinant.

In the generic case, however, the first and second quantized sign problems are not identical. For instance, the matrix element of $\widetilde{\mathbf{H}}_D$ between two determinants D and D_{ab}^{ij}, where D_{ab}^{ij} is obtained from D by replacing the single-particle orbitals ϕ_a and ϕ_b by ϕ_i and ϕ_j without re-ordering, is[8–10]

$$-\Big|\langle ij|\hat{u}_{12}|ab\rangle - \langle ij|\hat{u}_{12}|ba\rangle\Big|, \tag{10}$$

where $\hat{u}_{12}$ is the two-particle interaction operator, e.g., the Coulomb interaction $\hat{u}_{12} = 1/|\mathbf{r}_1 - \mathbf{r}_2|$. The equivalent element of $\widetilde{\mathbf{H}}_F$ in a permanent basis is

$$-\Big|\langle ij|\hat{u}_{12}|ab\rangle\Big| - \Big|\langle ij|\hat{u}_{12}|ba\rangle\Big|. \tag{11}$$

In general, these two matrix elements will not be equivalent. As a concrete example, consider a gas of four electrons at a density of $r_s = 1$ a.u. subject to periodic boundary conditions. Table I shows the ground state energy eigenvalues of the matrices obtained when this system is studied using a basis of (antisymmetrized) product functions constructed from a set of 38 one-electron plane waves. The sign problem in a basis of determinants is less severe than that in a basis of Hartree products.

$M_{\mathbf{ij}}$	Lowest eigenvalue (a.u.)
$(\mathbf{H}_F)_{\mathbf{ij}} = \langle \mathbf{i}\vert\widehat{H}\vert\mathbf{j}\rangle$	5.63133019
$(\widetilde{\mathbf{H}}_F)_{\mathbf{ij}} = -\vert\langle \mathbf{i}\vert\widehat{H}\vert\mathbf{j}\rangle\vert$	5.26282782
$(\mathbf{H}_D)_{D_\mathbf{i}D_\mathbf{j}} = \langle D_\mathbf{i}\vert\widehat{H}\vert D_\mathbf{j}\rangle$	5.63133019
$(\widetilde{\mathbf{H}}_D)_{D_\mathbf{i}D_\mathbf{j}} = -\vert\langle D_\mathbf{i}\vert\widehat{H}\vert D_\mathbf{j}\rangle\vert$	5.34900281
$(\widetilde{\mathbf{H}}_F)_{P_\mathbf{i}P_\mathbf{j}} = -\frac{1}{4!}\sum_{\substack{\vert\mathbf{i}\rangle\in\vert P_\mathbf{i}\rangle \\ \vert\mathbf{j}\rangle\in\vert P_\mathbf{j}\rangle}} \vert\langle \mathbf{i}\vert\widehat{H}\vert\mathbf{j}\rangle\vert$	5.26282782

TABLE I. Lowest eigenvalues of various matrices $M_{\mathbf{ij}}$ related to the sign problem in the 3D uniform electron gas.[6] Periodic boundary conditions were applied to a simulation cell of dimensions $L \times L \times L$ containing four electrons at a density of $r_s = 1$ a.u. The basis set consisted of all 38 plane waves with momentum less than $2\pi/L$. The resulting determinant and permanent Hilbert spaces each contain 567 functions with $M_s = 0$ and momentum $\mathbf{k} = \mathbf{0}$. The corresponding Hartree-product Hilbert space contains 13608 basis functions.

V. CONCLUSIONS

In summary, we have given two equivalent conditions for determining whether the first and second quantized sign problems for a given system are the same. For situations where the sign problems differ, we have shown that the second quantized algorithm is better. Thus, the use of an explicitly antisymmetrized basis can ameliorate the most fundamental problem faced by almost all fermion QMC methods: the sign problem. Indeed, our conditions show that this improvement *will* occur for nearly all problems involving QMC on realistic systems (atoms, molecules, solids, etc.). However, we have also seen that there are a number of lattice models of great interest to the condensed matter community, such as the Hubbard model, where second quantization has no effect on the sign problem.

There remain many open questions regarding the sign problem in FCIQMC. It has now been shown that both annihilation and second quantization improve the sign problem, but their relative effectiveness remains uncertain in general. Another interesting question is how the improved sign problem in FCIQMC compares to the fermion Monte Carlo (FMC) method introduced by Kalos and Pederiva[11], which uses correlated walks to enhance annihilation. In this latter method, Assaraf et al.[5] showed that the cancellation step similarly modifies the eigenvalue toward which FMC is unstable. Based on the results of these papers, one might then expect that combining correlated walks with second quantization in certain systems (e.g., the UEG in momentum space) might further attenuate the effects of the fermion sign problem.

Finally, we note that although our arguments and proofs have been focused on the case of fermions, they can be readily extended to many-boson systems and used to show that working in a second quantized basis of permanents is at least as good as working in a first quantized basis of Hartree products.

Appendix A: Proof of equivalence conditions

We will now show: a) that the conditions described in the main text uniquely characterize when the first and second quantized sign problems differ, and b) that, if they differ, the second quantized sign problem is less severe. We work with matrices formed from the operator $\widehat{U}$ introduced in the main text, such that the wave functions sampled at time steps n and $n+1$ are related by $|\psi_{n+1}\rangle = \widehat{U}|\psi_n\rangle$. We continue to use the notation $\widetilde{\mathbf{U}}_\alpha$ to denote a matrix whose elements are the absolute values of those in $\mathbf{U}_\alpha$, i.e.,

$$\begin{aligned} \langle \mathbf{i}\vert\widetilde{\mathbf{U}}_F\vert\mathbf{j}\rangle &= \left\vert\langle \mathbf{i}\vert\widehat{U}\vert\mathbf{j}\rangle\right\vert \\ \langle D_\mathbf{i}\vert\widetilde{\mathbf{U}}_D\vert D_\mathbf{j}\rangle &= \left\vert\langle D_\mathbf{i}\vert\widehat{U}\vert D_\mathbf{j}\rangle\right\vert \\ \langle P_\mathbf{i}\vert\widetilde{\mathbf{U}}_P\vert P_\mathbf{j}\rangle &= \left\vert\langle P_\mathbf{i}\vert\widehat{U}\vert P_\mathbf{j}\rangle\right\vert . \end{aligned} \tag{A1}$$

We have already shown in the main text that **if Eq. (7) holds, then the first and second quantized sign problems are identical.** The remainder of this appendix will proceed to prove the following statements:

- The conditions in Eq. (7) can be restated in terms of first quantized matrix elements (Eq. (A6)).
  - Therefore, if Eq. (A6) holds, then the first and second quantized sign problems are identical.
- If the conditions in Eq. (A6) do not hold, then the second quantized sign problem is strictly better than the first quantized sign problem.
  - Therefore, the first and second quantized sign problems are identical if and only if Eq. (A6) holds.

1. Restatement of conditions for equivalence

As noted in Eq. (7) from the main text, it is clear that the first and second quantized FCIQMC algorithms have the same sign problem if

$$\langle P_\mathbf{i}\vert\widetilde{\mathbf{U}}_F\vert P_\mathbf{j}\rangle = \langle D_\mathbf{i}\vert\widetilde{\mathbf{U}}_D\vert D_\mathbf{j}\rangle . \tag{A2}$$

Noting that the permanent $|P_\mathbf{j}\rangle$ and determinant $|D_\mathbf{j}\rangle$ occupy the same set of orbitals, we can expand them as

$$|P_\mathbf{j}\rangle = \frac{1}{\sqrt{N!}}\sum_{\mathbf{j}\in D_\mathbf{j}} |\mathbf{j}\rangle , \quad |D_\mathbf{j}\rangle = \frac{1}{\sqrt{N!}}\sum_{\mathbf{j}\in D_\mathbf{j}} |\mathbf{j}\rangle \ \mathrm{sgn}\langle \mathbf{j}|D_\mathbf{j}\rangle . \tag{A3}$$

Then, using Eqs. (A1) and (A3), Eq. (A2) can be rewritten

$$\begin{aligned} \langle D_{\mathbf{i}}|\widetilde{\mathbf{U}}_D|D_{\mathbf{j}}\rangle &= \langle P_{\mathbf{i}}|\widetilde{\mathbf{U}}_F|P_{\mathbf{j}}\rangle \\ &\Updownarrow \\ \left|\langle D_{\mathbf{i}}|\widehat{U}|D_{\mathbf{j}}\rangle\right| &= \frac{1}{N!}\sum_{\substack{\mathbf{i}\in D_{\mathbf{i}}\\ \mathbf{j}\in D_{\mathbf{j}}}} \langle \mathbf{i}|\widetilde{\mathbf{U}}_F|\mathbf{j}\rangle \\ &\Updownarrow \\ \left|\sum_{\substack{\mathbf{i}\in D_{\mathbf{i}}\\ \mathbf{j}\in D_{\mathbf{j}}}} \langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{i}|D_{\mathbf{i}}\rangle \mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle\right| &= \sum_{\substack{\mathbf{i}\in D_{\mathbf{i}}\\ \mathbf{j}\in D_{\mathbf{j}}}} \left|\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle\right| \ . \end{aligned} \tag{A4}$$

By the triangle inequality, the right-hand side of Eq. (A4) is greater than or equal to the left-hand side, with equality if and only if all terms within the absolute values on the left-hand side are of the same sign, $s_{D_{\mathbf{i}}D_{\mathbf{j}}}$. Since equality does hold, it follows that, for all $\mathbf{i} \in D_{\mathbf{i}}$ and $\mathbf{j} \in D_{\mathbf{j}}$, then either

- $\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle = 0$, or
- $\mathrm{sgn}\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{i}|D_{\mathbf{i}}\rangle \mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle = s_{D_{\mathbf{i}}D_{\mathbf{j}}}$,

(A5)

where the sign $s_{D_{\mathbf{i}}D_{\mathbf{j}}}$ is the same for all $\mathbf{i} \in D_{\mathbf{i}}$ and $\mathbf{j} \in D_{\mathbf{j}}$. If we consider two distinct FQ basis elements $\mathbf{j}, \mathbf{j}' \in D_{\mathbf{j}}$, we deduce that either

- $\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle = 0$ or
- $\langle \mathbf{i}|\widehat{U}|\mathbf{j}'\rangle = 0$ or
- $\mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle \mathrm{sgn}\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle = \mathrm{sgn}\langle \mathbf{j}'|D_{\mathbf{j}}\rangle \mathrm{sgn}\langle \mathbf{i}|\widehat{U}|\mathbf{j}'\rangle$.

(A6)

Note that these are precisely the conditions we assumed were met by the first quantized psip distribution in the main text (cf. Fig. 1).

We have now shown that **the conditions in Eq. (7) and Eq. (A6) are equivalent**. As a corollary, **if the conditions in Eq. (A6) hold, then the first and second quantized sign problems are identical.**

2. If Eq. (A6) is false, then second quantized is better than first quantized

We now prove that, if the conditions in Eq. (A6) are not met, then the sign problem in a second quantized basis is less severe than the sign problem in a first quantized basis. Therefore, for the remainder of this section, assume that Eq. (A6) does not hold.

Let $|\widetilde{\varphi}_D\rangle$ be the eigenstate of $\widetilde{\mathbf{U}}_D$ with the largest eigenvalue $\widetilde{t}_D$. Construct the (normalized) FQ state $|\varphi_F\rangle$ with components

$$\langle \mathbf{i}|\varphi_F\rangle = \frac{1}{\sqrt{N!}}\langle D_{\mathbf{i}}|\widetilde{\varphi}_D\rangle \ , \tag{A7}$$

where $|\mathbf{i}\rangle \in |D_{\mathbf{i}}\rangle$. Since $\widetilde{\mathbf{U}}_D$ is a non-negative real symmetric matrix, all amplitudes $\langle D_{\mathbf{i}}|\widetilde{\varphi}_D\rangle$ (and thus $\langle \mathbf{i}|\varphi_F\rangle$) have the same sign and may be chosen real and non-negative.

Now consider the expectation value $\widetilde{t}'_F$ of the matrix $\widetilde{\mathbf{U}}_F$ in the state $|\varphi_F\rangle$:

$$\widetilde{t}'_F \equiv \langle \varphi_F|\widetilde{\mathbf{U}}_F|\varphi_F\rangle = \sum_{\mathbf{i},\mathbf{j}} \langle \varphi_F|\mathbf{i}\rangle\langle \mathbf{i}|\widetilde{\mathbf{U}}_F|\mathbf{j}\rangle\langle \mathbf{j}|\varphi_F\rangle \ . \tag{A8}$$

From Eq. (A1), $\langle \mathbf{i}|\widetilde{\mathbf{U}}_F|\mathbf{j}\rangle = \left|\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle\right|$. Hence

$$\begin{aligned} \widetilde{t}'_F &= \frac{1}{N!}\sum_{\mathbf{i},\mathbf{j}} \langle D_{\mathbf{i}}|\widetilde{\varphi}_D\rangle\langle D_{\mathbf{j}}|\widetilde{\varphi}_D\rangle \left|\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle\right| \\ &= \frac{1}{N!}\sum_{D_{\mathbf{i}},D_{\mathbf{j}}} \langle D_{\mathbf{i}}|\widetilde{\varphi}_D\rangle\langle D_{\mathbf{j}}|\widetilde{\varphi}_D\rangle \sum_{\mathbf{i}\in D_{\mathbf{i}}}\sum_{\mathbf{j}\in D_{\mathbf{j}}} \left|\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle\right| \ . \end{aligned} \tag{A9}$$

In the last step, we have explicitly broken the sums over $\mathbf{i}$ and $\mathbf{j}$ into sums over determinants $D_{\mathbf{i}}$ and $D_{\mathbf{j}}$ and sums over the Hartree products contained in those determinants:

$$\sum_{\mathbf{i}} = \sum_{D_{\mathbf{i}}}\sum_{\mathbf{i}\in D_{\mathbf{i}}} \ . \tag{A10}$$

Since, by assumption, the conditions in Eq. (A6) are not met, for at least one $D_{\mathbf{j}}$ there must exist some $\mathbf{j}, \mathbf{j}' \in D_{\mathbf{j}}$ such that

- $\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \neq 0$ and
- $\langle \mathbf{i}|\widehat{U}|\mathbf{j}'\rangle \neq 0$ and
- $\mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle \mathrm{sgn}\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \neq \mathrm{sgn}\langle \mathbf{j}'|D_{\mathbf{j}}\rangle \mathrm{sgn}\langle \mathbf{i}|\widehat{U}|\mathbf{j}'\rangle$.

(A11)

Consider the term

$$\sum_{\mathbf{j}\in D_{\mathbf{j}}} \left|\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle\right| \tag{A12}$$

appearing on the right-hand side of Eq. (A9). Since $\langle \mathbf{j}|D_{\mathbf{j}}\rangle \neq 0$, this summation is equal to

$$\sum_{\mathbf{j}\in D_{\mathbf{j}}} \left|\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle\right| . \tag{A13}$$

Eq. (A11) tells us that the signs of the $\mathbf{j}$ and $\mathbf{j}'$ contributions to this summation differ before the absolute value is taken. Hence, by the triangle inequality,

$$\sum_{\mathbf{j}\in D_{\mathbf{j}}} \left|\langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle\right| > \left|\sum_{\mathbf{j}\in D_{\mathbf{j}}} \langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle\right| \ ,$$

and therefore, substituting back into Eq. (A9),

$$\widetilde{t}'_F > \frac{1}{N!}\sum_{D_{\mathbf{i}},D_{\mathbf{j}}} \langle D_{\mathbf{i}}|\widetilde{\varphi}_D\rangle\langle D_{\mathbf{j}}|\widetilde{\varphi}_D\rangle \sum_{\mathbf{i}\in D_{\mathbf{i}}} \left|\sum_{\mathbf{j}\in D_{\mathbf{j}}} \langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{j}|D_{\mathbf{j}}\rangle\right| . \tag{A14}$$

Noting that $[\widehat{H},\mathcal{A}]$ (which implies that $[\widehat{U},\mathcal{A}]=0$) and that

$$\sum_{\mathbf{j}\in D_\mathbf{j}} |\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{j}|D_\mathbf{j}\rangle = \sqrt{N!}|D_\mathbf{j}\rangle \ , \tag{A15}$$

we have

$$\begin{aligned}
\Big|\sum_{\mathbf{j}\in D_\mathbf{j}} \langle \mathbf{i}|\widehat{U}|\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{j}|D_\mathbf{j}\rangle\Big| &= \Big|\sqrt{N!}\langle \mathbf{i}|\widehat{U}|D_\mathbf{j}\rangle\Big| \\
&= \Big|\sqrt{N!}\langle \mathbf{i}|\widehat{U}\mathcal{A}|D_\mathbf{j}\rangle\Big| \\
&= \Big|\sqrt{N!}\langle \mathbf{i}|\mathcal{A}\widehat{U}|D_\mathbf{j}\rangle\Big| \\
&= \Big|\langle D_\mathbf{i}|\widehat{U}|D_\mathbf{j}\rangle \mathrm{sgn}\langle \mathbf{i}|D_\mathbf{i}\rangle\Big| \\
&= \Big|\langle D_\mathbf{i}|\widehat{U}|D_\mathbf{j}\rangle\Big| \ .
\end{aligned} \tag{A16}$$

We may now rewrite Eq. (A14) in terms of determinants

$$\widetilde{t}_F' > \frac{1}{N!}\sum_{D_\mathbf{i},D_\mathbf{j}} \langle D_\mathbf{i}|\widetilde{\varphi}_D\rangle\langle D_\mathbf{j}|\widetilde{\varphi}_D\rangle \sum_{\mathbf{i}\in D_\mathbf{i}} \Big|\langle D_\mathbf{i}|\widehat{U}|D_\mathbf{j}\rangle\Big| . \tag{A17}$$

The sum over $\mathbf{i}\in D_\mathbf{i}$ cancels the $1/N!$ prefactor to give

$$\begin{aligned}
\widetilde{t}_F' &> \sum_{D_\mathbf{i}D_\mathbf{j}} \langle D_\mathbf{i}|\widetilde{\varphi}_D\rangle\langle D_\mathbf{j}|\widetilde{\varphi}_D\rangle \Big|\langle D_\mathbf{i}|\widehat{U}|D_\mathbf{j}\rangle\Big| \\
&= \sum_{D_\mathbf{i}D_\mathbf{j}} \langle D_\mathbf{i}|\widetilde{\varphi}_D\rangle\langle D_\mathbf{j}|\widetilde{\varphi}_D\rangle\langle D_\mathbf{i}|\widetilde{\mathbf{U}}_D|D_\mathbf{j}\rangle = \widetilde{t}_D .
\end{aligned} \tag{A18}$$

Therefore, by the variational principle, the largest eigenvalue $\widetilde{t}_F$ of $\widetilde{\mathbf{U}}_F$ is greater than the largest eigenvalue $\widetilde{t}_D$ of $\widetilde{\mathbf{U}}_D$, meaning that **if Eq. (A6) does not hold, then the first quantized sign problem is strictly worse than the second quantized sign problem**.

3. Conclusions

In conclusion, we have shown that $\widetilde{t}_F = \widetilde{t}_D$ if and only if the conditions in Eq. (A6) hold. If they do not hold, then $\widetilde{t}_F > \widetilde{t}_D$. The second quantized sign problem is therefore less severe than the first quantized sign problem unless the conditions in Eq. (A6) are satisfied. Finally, we reiterate that, as long as the largest eigenvalues of $\mathbf{H}$ and $\widetilde{\mathbf{H}}$ are finite, their ground states are the same as the dominant eigenstates of $\mathbf{U}=\mathbf{I}-\mathbf{H}\Delta\tau$ and $\widetilde{\mathbf{U}}=\mathbf{I}-\widetilde{\mathbf{H}}\Delta\tau$, respectively, in the limit $\Delta\tau\to 0$. Therefore, for FCIQMC and LRDMC, the statements in this appendix can be recast in terms of ground state properties of the Hamiltonian matrix.

[1] W. M. C. Foulkes, L. Mitas, R. J. Needs, and G. Rajagopal, Rev. Mod. Phys. **73**, 33 (2001).
[2] G. H. Booth, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **131**, 054106 (2009).
[3] J. S. Spencer, N. S. Blunt, and W. M. C. Foulkes, J. Chem. Phys. **136**, 054110 (2012).
[4] M. Casula, C. Filippi, and S. Sorella, Phys. Rev. Lett. **95**, 100201 (2005).
[5] R. Assaraf, M. Caffarel, and A. Khelif, J. Phys. A: Math. Theor. **40**, 1181 (2007).
[6] Code available at `https://github.com/jsspencer/toy_fci`.
[7] Consider, for example, the case where $\mathbf{D}_\mathbf{i}$ and $\mathbf{D}_\mathbf{j}$ differ by a single orbital, such that ϕ_i is an orbital occupied in $\mathbf{D}_\mathbf{i}$, ϕ_j is in $\mathbf{D}_\mathbf{j}$, and ϕ_a is in both determinants. If only one integral is non-zero, e.g., the exchange integral $\langle ia|\hat{u}_{12}|aj\rangle$, then the off-diagonal terms of Eq. (7) are given by $\langle D_\mathbf{i}|\widetilde{\mathbf{H}}_D|D_\mathbf{j}\rangle = \langle P_\mathbf{i}|\widetilde{\mathbf{H}}_F|P_\mathbf{j}\rangle = -\big|\langle ia|\hat{u}_{12}|aj\rangle\big|$.
[8] J. C. Slater, Phys. Rev. **34**, 1293 (1929).
[9] E. U. Condon, Phys. Rev. **36**, 1121 (1930).
[10] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover Publications, 1996).
[11] M. H. Kalos and F. Pederiva, Phys. Rev. Lett. **85**, 3547 (2000).