Full-Dimensional Schrödinger Wavefunction Calculations using Tensors and Quantum Computers: the Cartesian component-separated approach

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Traditional methods in quantum chemistry rely on Hartree-Fock-based Slater-determinant (SD) representations, whose underlying zeroth-order picture assumes separability by particle. Here, we explore a radically different approach, based on separability by Cartesian component, rather than by particle [J. Chem. Phys., 2018, 148, 104101]. The approach appears to be very well suited for 3D grid-based methods in quantum chemistry, and thereby also for so-called “first-quantized” quantum computing. We first present an overview of the approach as implemented on classical computers, including numerical results that justify performance claims. In particular, we perform numerical calculations with four explicit electrons that are equivalent to full-CI matrix diagonalization with nearly $10^{15}$ SDs. We then present an implementation for quantum computers, for which both the number of qubits, and the number of quantum gates, may be substantially reduced in comparison with other quantum circuitry that has been envisioned for implementing first-quantized “quantum computational chemistry” (QCC).

1 Introduction

The importance of quantum chemistry simulation across a broad swathe of science and engineering lies beyond question. In the field of quantum computational chemistry (QCC)—i.e., quantum chemistry run on quantum computers—most efforts to date have attempted to simply “translate” as much as possible of the standard electronic structure methodology, developed over many decades for classical computers. Given the vast and fundamental differences between quantum and classical architectures, however, this may not be the most profitable or natural approach.

In particular, standard methods (what in the QCC parlance are often called “second-quantized,” in a sense to be defined shortly) rely on Hartree-Fock (HF) or other Slater-determinant (SD) basis set representations. The underlying zeroth-order picture assumes separable products of single-particle molecular (spin)-orbital functions. Depending on the further approximations used by the particular implementation, standard methods are:

(a) not always reliably accurate for strongly correlated systems (except in a full-CI matrix calculation that can be difficult to achieve in practice).

(b) generally not designed to compute many accurate excited electronic states (i.e., tens or hundreds of states, including position-dependent wavefunctions).

(c) not directly applicable to the combined electron-nuclear motion quantum many-body problem (describing the total molecule).

(d) not generally regarded as the most viable candidates for long-term, full-fledged quantum computing simulation.

In the QCC context, standard second-order methods are being pursued as an important but near-term strategy—e.g., for use on hybrid quantum/classical computing platforms.

In the long term, the most effective QCC algorithms are likely to be first-quantized strategies—i.e., those that rely on explicit coordinate-grid-based representations of the entire electronic (or electron-nuclear) wavefunction, across all system coordinates. Note that we are using “first-” and “second-quantized” in the QCC sense, which differs slightly from standard electronic structure usage, as has caused some confusion in the past. To make matters worse, in the QCC context, the term “first-quantized” can also be used to describe plane-wave and more sophisticated basis set representations, similar to the molecular orbitals of the second-quantized approach. However, insofar as QCC and this paper are concerned, the defining feature of any “second-quantized” calculation is its reliance on an SD basis representation. First-quantized methods are not constrained in...
this manner, and thereby not necessarily subject to the limitations (a) through (d) above. This issue is taken up again in Sec. 2.

In comparison with second-quantized methods, the chief drawbacks of first-quantized methods are that: (i) *much* larger basis set sizes are typically needed to represent the electronic wavefunction (at least for grid-based representations), and; (ii) antisymmetry is not “built in” from the start, but must be explicitly imposed. These present very substantial obstacles on classical computers, so much so that to date, only a few serious attempts have been made to develop viable first-quantized electronic structure methods (mostly in the context of two-electron basis functions or geminals). 36–40 The primary reason is the implied exponential scaling of computational resources with respect to the number of particles (N), or system dimensionality (3N).

On true quantum computers, however—at least as they are currently envisioned to exist within a few years—neither drawback (i) nor (ii) above is expected to be especially daunting. With regard to (i), the exponential scaling becomes linear scaling—at least in terms of the total number of logical qubits required to store the wavefunction (the algorithmic scaling is at worst polynomial in N). More specifically, storing the wavefunction will require something like 3N/log N logical qubits (ignoring ancilla qubits, error correction qubits, etc.), with a minimum of N ≈ 7. As for (ii), this is taken up in Sec. 2.4 All in all, first-quantized circuit-based QCC methods are regarded to be more likely than second-quantized circuits to achieve “quantum supremacy” 13,18,31,35—by which is meant, a calculation that would be impossible using the most advanced classical computers.

It has also been argued that first-quantized calculations are more accurate than second-quantized (apart from full-CI) calculations, as fewer approximations and assumptions are relied upon. 13,35 Though likely largely true, this author is not fully convinced by such arguments; in particular, grid-based calculations can introduce errors of their own—e.g., if a quadrature approximation is used. 41,47 On the other hand, it is certainly true that removing the SD constraint from the basis set opens the door to new types of highly efficient representations for handling strongly correlated systems, as deserves future exploration (Sec. 2.4).

First-quantized methods also enable direct treatment of the combined electron-nuclear motion quantum many-body problem—which is simply not possible in a second-quantized SD treatment. 13 This feature turns out to be *vital* important in the QCC context, owing to the fact that separate electronic and nuclear motion calculations require large-dimensional potential energy surfaces, whose explicit calculation itself scales exponentially—even on a quantum computer. 14,17,35 In contrast, a direct, first-quantized QCC calculation avoids this difficulty by solving the combined electron-nuclear problem “all at once.”

On the other hand, the tremendous promise of first-quantized QCC is mitigated by the limits of present-day quantum hardware, which can accommodate no more than ~100 or so qubits in total. 35 Of even greater concern is the limited number of quantum gates that can be reliably implemented within a quantum circuit—given current gate fidelities, and without viable error-correction or fault-tolerant strategies yet in play. 25,27,28,33,35,48,49 For realistic QCC applications, the circuit complexities required by first-quantized methods are still beyond what can be accommodated in the near future. Hence, first-quantized QCC is considered a “long-term” strategy, receiving far less attention to date than has second-quantized QCC. 21,24,35 Nevertheless by developing better first-quantized QCC algorithms today—i.e., with improved scaling, higher accuracy, fewer required qubits and quantum gates, etc.—we will arrive that much sooner at the desired tomorrow.

Recent efforts have concentrated on improving scaling and stability, 22,29,34,35 and on efficient strategies for implementing the requisite unitary evolutions [e.g., linear combination of unitary (LCU) operators]. 28,33,50–54 Additionally, Galerkin discretization offers a rigorously variational approach with respect to basis size 34,50,55 by eliminating all quadrature error. Such techniques represent the current state of the art in first-quantized QCC development, even when grid or plane-wave representations are used (second-quantized QCC has met with more success, to date, in terms of specialized orbitals/basis sets). 15,27,35,52,54

The present work approaches first-quantized QCC from a complementary direction—by exploiting alternate representations that may require fewer qubits, and may also give rise to quantum circuits with fewer quantum gates. Specifically, we employ a radically different, tensor-product representation of the exact Coulomb potential energy operators, based on separability by Cartesian component rather than by particle. 47,55,50 The resultant “Cartesian component-separated” (CCS) approach is necessarily first-quantized (by the definition given above), and otherwise turns out to resolve all of the limitations (a)–(d) as listed above) of the standard second-quantized SD methods.

On classical computers, the CCS tensor-product representation of the Hamiltonian may be combined with a similar tensor-product form for the wavefunction—giving rise to a highly efficient computational quantum chemistry scheme, exhibiting many orders-of-magnitude reduction in numerical effort, as compared to explicit representations. Using only grid or plane-wave basis sets, classical CCS calculations have been performed to compute multiple excited electronic states (including wavefunctions) for atoms up to lithium, 55–57 for other central-force applications with non-Coulomb interactions, 58 and for strongly correlated electron gases with up to N = 4 explicit electrons. 58,61 The method is also currently being applied to solve the combined electron-nuclear motion problem (for H2 62 and H3 63)—which has been identified as being important for long-term QCC, as discussed. 14,17,35

To further demonstrate the feasibility of the classical CCS approach, we have for this paper performed an explicit N = 4 calculation of the “harmonium” central-force system, 56,64,65 using only a plane-wave representation. The underlying basis size required is astronomical—i.e., N = 1015. This calculation may be compared with a full configuration interaction (full-CI) matrix diagonalization calculation conducted using a similar number of SD basis functions, and with M ≈ 5000 single-particle (spin)- orbitals.

Such classical CCS calculations are important not only in their own right, but also to establish accurate benchmarks for future first-quantized QCC calculations—particularly those using grid or plane-wave basis representations. On the other hand, the classical CCS calculations conducted to date may all be regarded as
“preliminary,” in the sense that they have all used a very poor choice of basis that does not exploit CCS’s primary advantages vis-à-vis correlation. In this paper, for the first time, we set the theoretical stage for “optimized” CCS representations (analogous to Hartree-Fock) that take maximum advantage of correlation, and may thus give rise to orders-of-magnitude reductions in the underlying basis size, $N_{\beta}$—irrespective of the subsequent tensor-product reductions that classical CCS also provides. Such developments are expected to greatly improve what classical CCS may ultimately be able to do—with respect to system size $N$, overall numerical accuracy, or both.

The remainder of this paper is as follows. In Sec. 2 we lay out the advantages and operation of the first-quantized CCS approach in more detail, discussing also the form of the tensor-product representations used for both the Hamiltonian operators and the wavefunctions. This section concludes with a discussion of permutation symmetry, and how to rigorously enforce the condition of antisymmetry. Sec. 3 analyzes various classical CCS results that have been obtained to date (including the brand new results for $N = 4$ harmonium), with an eye towards what these imply about the likely capabilities of the CCS approach in future, both in the classical and quantum computing contexts. Sec. 4 then lays out our proposed quantum circuitry for implementing CCS as a QCC method—encompassing both time-independent eigenstate solutions [via quantum eigensolvers such as quantum phase estimation (QPE)], as well as as time-dependent solutions.

Although it is likely that a CCS QCC approach could be applied in conjugation with more sophisticated unitary evolution strategies such as LCU [54] for pedagogical simplicity, we address here only the more standard and straightforward “canonical Trotter method.” [9,12,18,28,35] In this context, we can likely realize a reduction in the number of both qubits and quantum gates, in comparison with other first-quantized quantum circuitry that has been envisioned for QCC. Two alternate CCS implementations are presented, which can provide a potentially useful “engineering tradeoff” between quantum circuitry bottlenecks. Finally, future prospects are discussed, which turn out to hinge on (of all things) an efficient quantum implementation of the exponential function.

2 Methodology

2.1 Advantages of First Quantization and the CCS Approach

In order to better understand the “first-” vs. “second-quantized” terminology in the context of QCC, it is helpful to consider the corresponding quantum operators, as distinct from their basis set representations. In the traditional first-quantized formalism, the Hamiltonian operator is expressed using electron position coordinates as indicated in Eq. (5) itself—i.e., the position eigenstates. In principle, these are Dirac delta functions; in practice, due to basis set truncation, these are sinc functions [11,47] associated with a uniform lattice of grid points, and spanning the same Hilbert subspace as a corresponding band-limited set of plane waves. Both sinc (aka “plane-wave dual”) and plane-wave basis sets have been considered in the QCC context [13,24,26,55] and have also been employed with the CCS approach. However, we again emphasize that CCS offers tremendous flexibility in general, and a great many other choices of CCS basis set are also possible—including those for which substantial particle correlation is “built in” to the individual basis functions (Sec. 2.4).

What is not built in to any first-quantized approach, however, is antisymmetry—which, as noted, must therefore be explicitly imposed. Here, the second-quantized approach has the upper hand, essentially because it treats operators and basis functions on an equal footing [3]. In particular, second-quantized Hamiltonian operators are sums of products of creation and annihilation operators, acting on a set of $M \geq N$ single-particle (spin-)orbitals. Second quantized basis functions are “occupation number” (ON) vectors—i.e., binary strings denoting which of the $M$ orbitals are occupied—spanning the $2^N$-dimensional Fock space (in the “grand canonical” sense where $N$ may vary, although for all of our applications, $N$ is fixed). All ON vectors may be obtained by applying orbital-specific creation operators to the “vacuum state” of no electrons. The second-quantized approach is thus much more abstract and algebraic than the first-quantized approach, although at the end of the day, ON vectors always correspond to properly antisymmetrized SDs of single-particle orbitals. This is both an advantage (because antisymmetrization need not be dealt with explicitly) and a disadvantage (because no other type of basis may be considered).

The CCS approach as advocated here does not rely on SDs, single-particle orbitals, nor particle separability of any kind. It is therefore very much a first-quantized approach, by any reckoning. Using the representational basis, the Hamiltonian operator is (implicitly) represented as an $N_{\beta} \times N_{\beta}$ matrix, which is then diagonalized. In principle, a large number of accurately converged eigenstates may be obtained, with rigorous variational convergence to the exact results guaranteed in the complete basis set (CBS) limit. The approach may therefore be compared with full-CI matrix diagonalization calculations from the second-quantized realm [i.e., for which all $N_{\beta} = \binom{N}{M}$ possible SDs are retained]. However, CCS calculations are much more flexible than full CI—not only with respect to the choice of basis itself, but also in terms of how the basis is truncated. More specifically, in a full-CI calculation, $M$ is the only convergence parameter (with $M \rightarrow \infty$ defining the CBS limit). In contrast, in the CCS case, there are up to $3N$ (though usually just 3) separate basis truncation parameters, each of which can be adjusted independently for maximum efficiency.

There is one more advantage of the CCS approach that is particular relevant, especially for QCC. Since it is not limited to SDs, it can be applied directly to the combined electron-nuclear motion quantum many-body problem. Ordinarily, one imposes the Born-Oppenheimer (BO) approximation [12] to separate the electronic
and nuclear motion problems, although this introduces a source of error. More accurate results may therefore be obtained by solving the combined problem directly. In the QCC context however, there is a much more compelling and practical reason for wanting to solve the combined problem. This is because the BO approximation necessitates the development of an explicit potential energy surface (PES) over the entire 3N-dimensional space—a prospect which even on a quantum computer, scales exponentially with N [117,125]. By solving the combined electron-nuclear motion problem “all at once,” such PES problems are completely avoided—as are all BO-type errors.

The above considerations justify claims (a) thru (d) in Sec. 1 (although additional arguments are also provided throughout this paper). Going forward, we shall discuss both the CCS formalism itself, as well as its application to first-quantized QCC. Since both topics are likely unfamiliar to many readers, it is pedagogically useful to “divorce” them from each other. Accordingly, in this section we focus exclusively on the former, presenting an overview of how classical CCS is implemented, and explaining how it relates to—but differs from—conventional quantum chemistry methods.

The QCC case is then taken up again in Sec. 4. On the other hand, the past emphasis on plane-wave—or at least sinc—representations has played a significant role in the development of the QCC CCS implementation, both plane wave and sinc representations—a “worst-case” choice of basis indeed! Recognizing further that explicit matrix representations would require storage of $N_B^2 = L^{2N}$ elements in all, it becomes clear that even two-electron applications lie beyond what would be possible on any classical computer. Use of smarter CCS basis sets, not of the Eq. (2) form, can of course greatly reduce the requisite $M_d$ and $N_B$ sizes, thereby effectively increasing the number of electrons that might be treated explicitly. In any case, it is clear that the scaling of explicit vector and matrix representations with respect to $N$ poses a severe challenge for classical computers.

It is at this juncture, then, that the classical and quantum computational strategies part company—at least with respect to how the N-electron CCS wavefunction is actually represented numerically. On the quantum side, the exponential growth of $N_B$ with $N$ does not pose a fundamental problem; as discussed, this corresponds to linear growth in the number of qubits (Sec. 4). We therefore simply use the explicit vector representation of the N-electron wavefunction implied by Eq. (1), i.e.,

$$
\Psi(\vec{r}_1, \ldots, \vec{r}_N) \approx \sum_{m_1,=1}^{M_1} \cdots \sum_{m_N,=1}^{M_N} \Psi_{m_1, m_2, \ldots, m_N} \Phi_m(\vec{r}_1, \ldots, \vec{r}_N).$$

[Eq. (3)]

[together with Eq. (2), as is. More specifically, in the present QCC CCS implementation, both plane wave and sinc representations are used, with explicit storage of the vector, $\Psi_{m_1, m_2, \ldots, m_N}$, requiring $N_B = L^{3N}$ elements, as discussed. [As per Sec. 4, the quantum Fourier transform (QFT) is used to switch between these two representations.]

In contrast, the classical CCS implementation replaces the explicit vector representation of Eq. (3) with the following [generic Eq. (1) basis] tensor “sum of product” (SOP) form:

$$
\Psi_{\lambda}(\vec{r}_1, \ldots, \vec{r}_N) \approx \sum_{\lambda=1}^{\Lambda} \sum_{m_1,=1}^{M_1} \cdots \sum_{m_N,=1}^{M_N} \sum_{m,=1}^{M_m} \Psi_{\lambda}(\vec{r}_1, \ldots, \vec{r}_N).$$

[Eq. (4)]

[In Eq. (4), the number of elements to be stored is now only $\Lambda(M_x + M_y + M_z)$—which, in general, is only a tiny fraction of $N_B$. Of course—as with all tensor methods—this requires that a sufficiently good wavefunction approximation is achievable using a reasonably small number of terms, $\Lambda$. For all CCS applications to date, this has been achieved with $\Lambda$ on the order of 100 [47,55,56,61].]
Consequently, explicit \(N\)-electron wavefunctions have been stored using only a modest amount of RAM on classical computers—even up to \(N = 4\).

Such enormous reductions are not atypical when tensor SOPs are employed. Recent years have seen an explosion in the use of modern tensor methods across a vast range of data science applications, as a tool for drastically reducing data storage requirements.\[^{66}^{67}\] Even in the electronic structure realm, use of tensor SOPs to represent the electronic state is not new, and has been applied to great effect for a number of years now.\[^{62}^{63}\] Nevertheless, our use of tensor SOPs is radically different from earlier efforts, in two important ways. To begin with, it is applied across a CCS basis that is in general separable only by Cartesian component [Eq. (1)] and not by particle. The very nature of the tensor products involved is thus quite different from previous efforts based on particle-separated SD orbitals.

Secondly—and arguably more importantly—the CCS approach enables a novel tensor SOP representation of the exact, full \(N\)-electron Hamiltonian, that is remarkably efficient and accurate, and that can handle Coulombic singularities with ease—even in a sinc grid-based representation. This is because potential energy functions are not simply evaluated at the grid points. As a consequence, it is possible to place a grid point even directly on a Coulombic singularity, with no particularly damaging numerical repercussions.\[^{64}^{65}\] Likewise—and regardless of the particular CCS basis representation—the Hamiltonian tensor SOP is not some arbitrary numerical approximation to the explicit matrix representation, but is instead a fundamental identity that arises naturally from a CCS analysis of the underlying operators. This is described in detail in the following subsection.

### 2.3 CCS Tensor SOP Representation of the Hamiltonian

The first-quantized electronic structure Hamiltonian \(\hat{H}\) is generally of the form

\[
\hat{H} = \sum_{i=1}^{N} \left( \frac{\hat{p}_{i}^2}{2m_e} + \frac{\hat{p}_{i}^2}{2m_e} + \frac{\hat{p}_{i}^2}{2m_e} \right) + \sum_{i=1}^{N} V_{\text{ext}}(x_{i}, y_{i}, z_{i}) + \sum_{i<j} V_{\text{ee}}(x_{i}, y_{i}, z_{i}, x_{j}, y_{j}, z_{j}),
\]

where \(m_e\) is the mass of the electron. The first sum in Eq. (5) above represents the kinetic energy contribution, which separates by both particle and Cartesian component. The remaining, external \((V_{\text{ext}})\) and pair repulsion \((V_{\text{ee}})\) potential energy terms, respectively, involve three or six coordinates each. These are generally taken to have Coulombic form, although the present method is not necessarily restricted to Hamiltonians of this kind.

Assuming a Coulombic form for the electron pair repulsion contribution, we have

\[
V_{\text{ee}}(x_{i}, y_{i}, z_{i}, x_{j}, y_{j}, z_{j}) = V_{\text{ee}}(s) = 1/s^{1/2}, \quad \text{with} \quad s = (x_{i} - x_{j})^2 + (y_{i} - y_{j})^2 + (z_{i} - z_{j})^2.
\]

Inverse Laplace transformation then yields the following exact form:

\[
\hat{V}_{\text{ee}} = \frac{2}{\sqrt{\pi}} \int_0^\infty \hat{\gamma}(\beta) \hat{\gamma}(\beta) d\beta, \quad \text{where} \quad (7)
\]

\[
\hat{\gamma}(\beta) = \exp\left[-\beta^2(d_i - d_j)^2\right], \quad \text{where} \quad (8)
\]

In Eq. (7) above, the individual \(\gamma\) factors in the integrand (e.g., \(\hat{\gamma}(\beta) = \exp[-\beta^2(x_i - x_j)^2]\)) are two-particle operators involving just a single Cartesian component, \(d\). The critical point is that these factors separate by Cartesian component, and not by particle. Note that spherical symmetry implies the same form for all of the \(\hat{\gamma}(\beta)\), and so in practice the \(d\) subscript can sometimes be dropped.

A form similar to Eq. (7) has been used previously in electronic structure, in the context of Rys polynomial integrals.\[^{77}\] In that context, the component separability of Eq. (7) is exploited in order to simplify the evaluation of Coulomb and exchange integrals—a perennial, if well-established challenge in the electronic structure community. Here, however, the Cartesian component separability of the \(\beta\) integrand is used in an entirely different manner—i.e., to construct a natural tensor SOP representation of the two-electron pair repulsion operator itself. Also, Rys considered only Gaussian basis functions, i.e., not general CCS basis representations of the form of Eq. (4), and certainly not the tensor-SOP reduction [i.e., Eq. (4)].

To convert Eq. (7) above into an explicitly tensor-SOP form, the one-dimensional integral over \(\beta\) is evaluated numerically by quadrature, on a finite and discrete set of quadrature points, \(\beta_{\lambda}\). The integral is then effectively replaced with a tensor-product sum of the form

\[
\hat{V}_{\text{ee}} = \sum_{\lambda=1}^{\Lambda_{\text{ee}}} w_{\lambda} \hat{\chi}_{\lambda},
\]

where the \(w_{\lambda}\) are the quadrature weights [into which the \(2/\sqrt{\pi}\) factor from Eq. (7) has also been subsumed]. Remarkably, quadrature schemes with as few as \(\Lambda_{\text{ee}} = 22\) points have been found that provide accuracies near to machine precision, with substantially smaller \(\Lambda_{\text{ee}}\) values required for chemical accuracy (i.e., ~1–2 millihartree). To our knowledge, no particle-separated tensor-SOP matrix representations of \(V_{\text{ee}}\) provide comparable accuracy with as few terms.\[^{23}^{24}\] That said, recent graphically contracted function (GCF) and all configuration mean energy (ACME) methods show that such dramatic reductions are possible, at least in the multiconfiguration self-consistent field (MC-SCF, including complete active space or CASSCF) and state-averaged contexts.\[^{24}^{26}\]

The individual factors in Eq. (9) are two-particle single-component “potential energy” operators that get represented as single-component matrices as follows (e.g., for \(x\)):

\[
\chi_{n_{i}m_{i}} = (\beta_{\lambda}^2 | n_{i}, m_{i})\]

\[
= \int X_{n_{i}}^{*}(x_{1}, \ldots, x_{N}) e^{-\beta_{\lambda}^2(x_{i} - x_{j})^2} X_{m_{i}}(x_{1}, \ldots, x_{N}) dx_{1} \ldots dx_{N}\]

For basis functions that are also particle-separated as per Eq. (2) (e.g., plane waves), the integrals in Eq. (10) reduce to two dimen-
visions. Still simpler forms will be considered in Sec. 4 e.g. based on quadrature. Even for optimized, highly correlated CCS basis functions of the Eq. (1) form, the integrals of Eq. (10) can be efficiently integrated numerically—e.g., using a further tensor-SOP decomposition.

In any event, these CCS Coulomb integrals need only be performed once for all time, for a given choice of basis—irrespective of any subsequent electronic structure calculations to which they might be applied. Once the component tensor matrices have been determined as per above, they are used to construct a tensor-SOP representation of the electron pair repulsion contribution to the Hamiltonian operator that requires storage of at most \( \Lambda_{ee}(M_1^2 + M_2^2 + M_3^2) \) elements. For plane-wave and other particle-separated CCS basis sets of the Eq. (2) form, only \( \Lambda_{ee} L^4 \) elements need be stored.

There remain, in the Hamiltonian of Eq. (5), additional contributions from the kinetic energy, and the external potential energy, \( V_{ext} \). If the latter represents Coulomb attraction to nuclei—as is expected to be the most common case—then a CCS tensor SOP form very similar to Eq. (7) may be employed. Matrix elements are also defined similarly to Eq. (10). Storage requires \( \Lambda_{ee}(M_1^2 + M_2^2 + M_3^2) \) elements in the most general case—with \( \Lambda_{ee} \) about as small as \( \Lambda_{ee} \), despite the fact that the Coulomb interaction is now attractive. For CCS basis sets that are in addition particle-separated [Eq. (2)], the scaling is only \( \Lambda_{ee} L^2 \).

On the other hand, it must be recognized that attractive, bare Coulomb potentials tend to generate large errors when plane-wave or sinc basis representations are used. Stated differently, such basis sets represent a very inefficient choice when \( V_{ext}(\vec{r}) = -\sum Z_k/|\vec{r} - \vec{R}_k| \) for which \( L \) values in excess of 100 (or equivalently, \( M > 10^6 \)) may become required in order to attain chemical accuracy, as discussed. Better CCS basis sets, particularly highly correlated ones, will provide much better performance, in terms of either: (a) greatly reducing the overall basis size \( N_B \) needed to achieve a given level of accuracy, or; (b) greatly improving the numerical convergence accuracy for a given \( N_B \). This issue is taken up again in Secs. 2.4 and 3.

It should also be stated that Coulomb potentials are far from the only type for which a Laplace-transformed CCS SOP form can be obtained. In particular, Yukawa and long-range Ewald potentials have also been represented in this fashion. There are also, of course, external potentials that naturally adhere to the CCS form—such as isotropic harmonic oscillator potentials (i.e., “harmonium”), which have also been considered in this context (Sec. 3). Finally, we point out that the Cartesian kinetic energy operator itself [Eq. 5] is also naturally CCS, and therefore also straightforward and inexpensive to represent in a CCS basis. For further details, please consult [55] and [56], and also Secs. 3 and 4.

The discussion presented in this subsection primarily refers to how the various components of the Hamiltonian matrix of Eq. 5 are represented in tensor-SOP form on a classical computer. In particular, use of CCS tensor-SOP representations very dramatically reduces Hamiltonian matrix storage down from the \( N_B^2 \) elements that would otherwise have to be stored in an explicit representation. Similarly dramatic savings using a CCS tensor-SOP representation for the wavefunction vector then make it feasible to perform explicit \( N \)-electron calculations on a classical computer—to chemical accuracy, even for strongly correlated systems, and for highly excited electronic states, including wavefunctions—at least up to \( N = 4 \) or so. This is the story, more or less, on the classical computing side.

For the quantum computing implementation, however, things are rather different. Whereas on a quantum computer, qubits are indeed used to represent the wavefunction (albeit explicitly, rather than in tensor-SOP form), the Hamiltonian matrix elements per se are not stored. Instead, the action of the Hamiltonian on the wavefunction is simulated through the use of appropriate quantum circuitry—i.e., a collection of quantum gates—applied to the set of logical qubits used to represent \( \Psi \).

It is worth reflecting on the fundamental differences between the basic QCC framework as described above, and that of traditional linear algebra as implemented on classical computers. In the latter context, a (direct) matrix–vector product is pretty much always implemented numerically in the same way, regardless of the choice of basis used to represent the matrix. Of course, the matrix itself must be stored explicitly, in addition to the vector, and it is in these explicit representations that one encounters variations from one basis set to another. In the QCC context, however, the Hamiltonian matrix is reflected in the form of the quantum circuitry itself—which consequently changes, depending on the choice of basis set. Even for a given basis, there can be many different strategies, all designed to perform the same operation more or less, but using different quantum circuitry. In any event, the QCC algorithm proposed in this work (Sec. 4) certainly differs from previous quantum circuitry designed to do the same thing. In large measure, this is because it is based on the CCS tensor-SOP representation of \( \hat{H} \), as described in this subsection, but there are some other new wrinkles as well.

### 2.4 Spin, Permutation Symmetry, and Enforcement of Rigorous Antisymmetry

Due to the Pauli Exclusion Principle, the entire \( N \)-electron wavefunction (including spatial and spin components) must be antisymmetric with respect to exchange of any two electrons. More properly, the wavefunction must belong to the totally antisymmetric (\( A_2 \)) irreducible representation (irrep) of the \( N \)-body permutation group, \( S_N \). In the standard particle-separated approach, SDs are used to automatically enforce rigorous antisymmetry of the entire electronic wavefunction. This generally requires that spin states are built into the definition of the single-electron states (spin-orbitals). since our CCS methodology is not based on SDs, some other means must be adopted to enforce rigorous antisymmetry of the entire electronic wavefunction.

Spatial-spin decompositions are fundamental to a wavefunction approach to electronic structure. For this paper, we shall always assume that the entire \( N \)-electron wavefunction can be written as the product of an overall spatial wavefunction times an overall spin state. This spatial-spin factorization is legitimate for the Hamiltonians considered here, which do not involve spin explicitly (although the methodology could certainly be generalized
to accommodate spin-orbit coupling or other corrections stemming from the Dirac equation). As a consequence, spin never enters into our numerical calculations at all, so that only the spatial part of the electronic wavefunction is ever explicitly represented (e.g., in Sec. 2.2). Each computed numerical energy level would therefore have a $2^N$-fold spin degeneracy, were it not for antisymmetry.

Conversely, the spin factor plays a huge role in determining which spatial wavefunctions can give rise to entire wavefunctions that are antisymmetric. More generally, spin is used to determine the spin degeneracies of the computed electronic states. This is achieved using group theory, as follows. First, for a given permutation group, $S_N$, the direct-product group (representing the entire wavefunction) is determined. Next, the $2^N$-dimensional spin representation is decomposed into its $S_N$ irreps. Based on available spin irreps and degeneracies, and the direct-product table, the corresponding allowed spatial irreps and entire wavefunction degeneracies are determined.

In the two-electron case, this is rather trivial: spatially symmetric ($\hat{A}_1$) solutions correspond to spin-singlet ($A_\Sigma$) states, and spatially antisymmetric ($\hat{A}_2$) solutions to spin-triplet ($A_\Pi$) states, as per the standard and familiar rules. Thus, numerically computed (spatial) states for both $S_2$ irreps are physically realized. For larger $N$, however, the situation becomes much more complicated, in accord with the corresponding permutation symmetry groups, $S_N$. For one thing, not all of the $S_N$ irreps are physically realized for $N > 2$. Additionally, there are degenerate irreps that appear, with far less trivial representations in terms of the underlying product basis. The direct-product tables are also decidedly more complicated. Nevertheless, the requisite group theory has been worked out by us, for all cases up to $N \leq 6$.

| $N$ | $2^N$ | Spin irrep decomposition | Spatial irreps |
|-----|-------|--------------------------|---------------|
| 2   | 4     | $3A_2 \oplus A_1$       | $A_1, A_2$    |
| 3   | 8     | $4A_1 \oplus 2E$        | $A_2, E$      |
| 4   | 16    | $5A_1 \oplus E \oplus 3T_2$ | $A_2, E, T_1$ |
| 5   | 32    | $6A_1 \oplus 4G_1 \oplus 2H_1$ | $A_1, G_2, H_2$ |
| 6   | 64    | $7A_1 \oplus 5H_1 \oplus 2H_2 \oplus 3I_1$ | $A_2, A_1, H_1, L_2, M_1, M_2$ |
|     |       |                          |               |

Let us begin with the $S_N$ irrep decompositions of the $2^N$-dimensional spin state representations. These are summarized in Table 1 Column III. Note that $A_2$ never appears in the spin state irrep decompositions, except for $N = 2$. This implies, e.g., that the $A_1$ spatial states are never physically realized for $N > 2$. More generally, from the direct product tables for $S_N$, we have ascertained exactly which spatial irreps can give rise to an overall $A_2$ state. The resultant physically realizable spatial irreps, and also the forbidden irreps, are listed in Columns IV and V, respectively, of Table 1. Note that irreps are labeled as follows. Labels $E, T, G, H, I$, etc., refer to irreps that are, respectively, two-, three-, four-, and five-fold degenerate, etc. For groups with more than one irrep of a given degeneracy, subscripts are assigned such that smaller numerical values correspond to more positive character under two-particle exchange.

From Table 1 it is clear that as $N$ increases, an increasingly small fraction of spatial states is allowed by permutation antisymmetry. Roughly speaking, this fraction is found to be 100%, 84%, 58%, 35%, and 18%, for $N = 2$–6, respectively. In order to exploit this situation as much as possible, symmetry adaptation of the CCS basis set may be utilized. This improves the efficiency of the calculations, by enabling each irrep to be computed independently of the others. Additionally, we need only perform calculations for those irreps that are physically realizable.

There are two modes in which symmetry adaptation of the basis can be implemented. The first pertains to a general CCS basis of the Eq. (1) form, for which the individual $X_{m_s}, Y_{m_s}$, and $Z_{m_s}$ factors are themselves $S_N$-symmetry adapted. This is the eventual goal, i.e., use of a CCS basis for which the individual component-wise factors are fully correlated across all $N$ particles, optimized for the specific application at hand, and symmetry-adapted. More specifically, the single-component, $X_{m_s}(x_1, \ldots, x_N)$, etc., basis functions will be obtained as the eigenstates of optimal “effective” component Hamiltonians, $H_{m_s}$, etc., which themselves are invariant under $S_N$. The effective component Hamiltonian problems have one-third the dimensionality of the full problem (and can themselves be symmetry-adapted), and are therefore presumed tractable.

Although perhaps a bit counterintuitive at first, the resultant “optimal CCS basis” (OCCSB) functions may be conceptualized as the component-based analog of the SCF orbitals. In other words, whereas the SCF molecular orbital solution is what naturally arises when one assumes only separability by particle, the OCCSB is what naturally arises when one assumes only separability by Cartesian component. From a practical computational perspective, the chief advantage in either case is the same: a greatly reduced separable basis size, in comparison, e.g., with a plane wave representation.

We can estimate the basis size reduction as follows. For an explicit plane-wave calculation, the basis size is $N_B = L^{3N}$. A plane-wave basis may be a reasonably good choice for certain applications, but for attractive external Coulomb potentials, it leads to $L \approx 100$ or so, as discussed (Sec. 2.3). For $N = 4$ or more, $N_B$ exceeds one mole in size. For an OCCSB, the basis size is $N_B = M_d^2$. For $N = 4$, we estimate that $M_d$ might be in the range 1000–10000, leading to as few as a “mere” billion total basis functions in all. This is well within reach classically; CCS calculations to date have been performed with from $10^{12}$ to $10^{18}$ basis functions—although basis size per se is not the only factor governing overall cost of the calculation. Further details are provided in an upcoming publication, with Sec. 3 of this paper also providing some new and compelling numerical evidence, in the context of the harmonium calculations.

In any event, for any CCS basis that respects component-wise $S_3$ symmetry (i.e., whether the OCCSB or not), symmetry adaptation for the final 3N-dimensional basis of Eq. (1) is straightforward to manage. In effect, each triple-Cartesian product implied by Eq. (1) has an $S_N$ character decomposition that can be determined using two applications of the $S_N$ direct-product table. In
practice then, one simply gathers together the triple-product basis functions for a given (physically allowed) irrep, and uses just those basis functions to construct a symmetry-adapted block of the Hamiltonian matrix.

The second mode of symmetry adaptation applies in cases where the $X_m(x_1, \ldots, x_N)$, etc., functions are not themselves symmetry-adapted. This is necessarily the case if the basis functions are also particle-separated, as in Eq. (2). In such cases, the basis functions naturally partition into equivalence classes for which the $N$ individual $m_{id}$ indices are identical, apart from permutations. It is then possible to create symmetry-adapted linear combinations from each such equivalence class, as follows:

(a) using the $S_N$ character table, construct the representation of the projection operator for each irrep, in the small set of basis functions in a given equivalence class; (b) apply each projection operator to each product basis function in turn, to construct the symmetry-adapted linear combinations.

The above procedure has been applied for the $N = 3$ and $N = 4$ applications presented in Sec. 3 which represent the first $N > 2$ CCS calculations ever performed. Although there are a number of possible scenarios (reminiscent of quantum statistics) a simple example will serve to clarify the procedure. Consider a set of $N = 3$ particle-separated basis functions of the Eq. (2) form, for which two of the three indices, $m_1$, $m_2$, and $m_3$, have the same value $m$, and the third has a different value $n \neq m$. This defines an equivalence class of three orthogonal basis functions, i.e.

$$\phi_1^m(x_1) \phi_2^m(x_2) \phi_3^n(x_3) = \langle x_1 x_2 x_3 | m m m \rangle$$

$$\phi_1^m(x_1) \phi_2^n(x_2) \phi_3^m(x_3) = \langle x_1 x_2 x_3 | m m n \rangle$$

$$\phi_1^n(x_1) \phi_2^m(x_2) \phi_3^m(x_3) = \langle x_1 x_2 x_3 | n m m \rangle$$

Construction and application of the irreps projection operators then results in one (unnormalized) linear combination with $A_1$ character, zero combinations with $A_2$ character, and two combinations forming an $E$ pair, as follows:

$$A_1 : \quad |m m m \rangle + |m m n \rangle + |n m m \rangle \quad (11)$$

$$E : \quad |m m m \rangle + |m m n \rangle - 2|m n m \rangle, \quad (12)$$

$$\quad |m n m \rangle - |m m m \rangle \quad (13)$$

On reflection, the permutation symmetry adaptation schemes used in the CCS context, as described above, are certainly much more complicated than the simple and familiar SD “work horse.” However, they are also much more flexible, as they can be applied to any possible combination of spin and spatial states, and moreover, need not be restricted to overall $A_2$ symmetry character. This last point is extremely important, vis-à-vis generalizing the CCS method for the combined electron-nuclear motion quantum many-body problem, wherein electrons and nuclei (be they fermions or bosons, identical or not) are treated on an equal footing. Such applications present a rich, group theoretical structure that cannot be properly addressed simply by using SDs. They are, however, easily amenable to the CCS symmetry adaptation tools as laid out in this subsection—thereby addressing point (c) from Sec. 1.

We conclude this subsection with a brief discussion of numerical contamination. On a classical computer, it is well-known that numerical roundoff error can introduce a tiny contribution from the wrong symmetry character into the wavefunction. Moreover, repeated applications, e.g. of the Hamiltonian acting on the wavefunction, can magnify this error exponentially.83,86 There is, however, a simple remedy for this problem as well; periodically, the projection operator for the desired irrep should be applied to the current wavefunction, to ensure its purity.

Intriguingly, the situation on a quantum computer is quite different. There are, first of all, various methods that have been devised for imposing rigorous antisymmetry on qubit representations of the electronic wavefunction, analogous to the procedures described above.47,55,56 Moreover, as in the classical computing case, small symmetry errors are to be expected. Interestingly, however, a recent, rigorous error bound characterization43 found that these errors do not grow exponentially with repeated applications. This is a quite important result, evidently due to the fact that all operations performed on a quantum computer are rigorously unitary—unlike the analogous operations on a classical computer. It is also quite fortuitous, as the implementation of projection operators that would otherwise be required to purify the wavefunction might pose a difficulty on a quantum computer, because projections are necessarily non-unitary.

3 Results: Classical Computing Benchmarks

The classical CCS algorithm has been implemented in the form of our computer code, Andromeda, and applied to several small benchmark applications, with $N = 2$, 3, and 4 explicit electrons.47,55,56,61 In every case to date, a plane-wave or sinc basis representation was used. Results for selected earlier and preliminary work are summarized in Sec. 3.1. In Sec. 3.2 we present results for the “harmonium” system (i.e., with harmonic external field $V_{ext}$), including earlier $N = 2$ calculations,55 together with new results for $N = 4$. Other prior or preliminary results, e.g. for long-range Ewald potentials59 for the $H_2$ and $H_3^+$ electronic structure problems, and for the $H_2$ and $H_3^+$ combined electron-nuclear motion problems,62,63 will not be discussed further here.

Collectively, the above model calculations are useful in their own right, but also in terms of what they reveal about prospects for the classical CCS methodology, once optimized OCCSB basis sets are employed instead of plane waves. The model calculations are also quite useful as benchmarks for first-quantized QCC calculations—providing more accurate estimates for the required number of qubits, for example, than the methods that have been relied upon in the past.

First, however, we provide a very brief overview of the classical CCS algorithm, as it is currently implemented in Andromeda. For a much more detailed exposition, please consult the references.47,55,56 To begin with, the CCS tensor-SOP representations for both the wavefunction vector and the Hamiltonian matrix have already been specified, in Eqs. (4) and (9), respectively. In-
so far as the algorithm is concerned, the main operation is a block Krylov subspace procedure, similar to Lanczos. This requires a sequence of matrix-vector products with the Hamiltonian. Since both matrix and vector are tensor SOPs, the operation is fast. On the other hand, the tensor-SOP rank—or number of terms, Λ, in the Eq. (4) sum—increases rapidly with each successive matrix-vector product. To curb this growth in Λ, the alternating least squares (ALS) approach of Beylkin and coworkers is used.

3.1 Summary of previous classical CCS results

**H Atom**: The simplest benchmark calculation possible is the hydrogen atom (N = 1). In Ref. [55], we computed the ground state energy of the non-relativistic H atom to an accuracy of ∼0.3 millihartree (i.e., much better than chemical accuracy). A bare Coulomb potential was used with a plane-wave basis, which constitutes a “worst-case” choice, as discussed. A single-coordinate basis size of L = 81 was required, corresponding to a second-order full-CI matrix diagonalization calculation with M = 531,441 orbitals and N₈ = 531,441 SDs.

**He Atom**: In the original study of Ref. [55], an explicit N = 2 calculation of the He atom was also performed, again with bare Coulomb potentials and a plane-wave basis. The greater Z = 2 attraction of the He nucleus as compared with H necessitates a somewhat finer grid. Moreover, energy excitation and partial screening demand larger coordinate ranges. Consequently, L = 101 is now required to converge the the lowest-lying dozen or so electronic states to chemical accuracy. This corresponds to a second-order full-CI matrix diagonalization calculation with M = 1,030,301 orbitals and N₂ = 1.0615 × 10^{12} SDs. Note that we are able to obtain the excited electronic energies (and wavefunctions) without expending any additional numerical effort beyond that required to obtain the ground state.

Finally, in more recent (unpublished) work, the plane wave basis was supplemented with additional Gaussians to better handle the cusp region. This enabled reduction of numerical convergence error to tens of millihartrees.

**Li Atom**: A first-quantized plane-wave calculation of the Li atom (N = 3) ground state energy has been touted as an important QCC benchmark. The main reasons are that: (a) the required number of logical qubits has been estimated to be at least 100, and may therefore not be very far beyond present-day limits of quantum hardware, and; (b) the classical calculation is believed to be intractable. Conversely, if the above Li atom calculation is actually possible on a classical computer, then this finding would be quite significant, because it would provide an important first-quantized QCC benchmark, while simultaneously pushing back the threshold for “quantum supremacy.”

Using our classical CCS code Andromeda, we have obtained preliminary results for the Li atom—again, treating all electrons explicitly, and using bare Coulomb potentials and a plane-wave basis. Our preliminary results suggest not only that a classical calculation is possible, but also that a chemically accurate QCC calculation (performed using exact γ matrices; see Sec. 4.3) should require only ∼60 logical qubits (3Nn = 63, with N = 3 and n = 7). This places the Li atom application within much closer reach of present-day quantum hardware than might have been imagined. On the other hand, our assertion is not yet fully confirmed, as it is based on an L = 101 (M = 1,030,301, N₈ = 1.0937 × 10^{18}) classical calculation that is not fully completed.

The reason is because of very slow convergence with respect to the number of Krylov subspace iterations. More specifically, we have not yet been able to achieve a convergence of the Li atom ground state energy to better than a few tens of millihartrees—it seems that a linear space of N₈ = 10^{18} dimensions is simply too large for such methods to operate effectively within. Note that memory limitations are decidedly not the issue here! Eqs. (4) and (9) have no difficulty reducing RAM requirements for such astronomical N₈ values down to a very modest size.

In any event, although the computed ground state energy is not yet Krylov-converged, there is an independent indication that the basis set convergence itself is sufficient to achieve at least near-chemical accuracy. More specifically, Andromeda has the capability to compute the total probability of a computed wavefunction along each of the 6N position coordinate edges (i.e., minimum and maximum dᵢ grid values), and also each of the 6N momentum space edges. According to this metric, the largest position-edge probability for the ground state wavefunction is 5.60 × 10^{-5}, whereas the largest momentum-edge probability is 2.36 × 10^{-8}. These values are on a par with similar basis-set converged calculations for He and H as described above.

**Correlated Electron Gas (CEG)**: The above examples clearly demonstrate that plane waves are not well suited for systems with attractive bare Coulomb potentials. Even so, we have been able to perform explicit all-electron calculations of this kind for systems with up to N = 3 and N₈ = 10^{18}. How much further could we scale up in N, if a more “competitive” basis such as OCGS were employed? Short of actually performing such calculations, the next best thing would be to find systems for which the plane-wave basis itself might be nearly optimal. For this purpose, the best application is probably the “correlated electron gas” system—i.e., with V_{ext} = 0, periodic boundary conditions, and a fixed number of electrons per unit cell (in contrast to the uniform electron gas or “jellium” mode).

Using Ewald summations, we are computing exchange-correlation energies for the correlated electron gas system with N = 2, 3, and 4 explicit electrons, for both spin-restricted and spin-unrestricted cases. An extremely broad range of Wigner-Seitz radii is being considered, ranging from metallic to Wigner crystal regimes where correlation effects dominate. This project is still ongoing. However, the best indication is that L = 11 suffices for most Wigner-Seitz radius values. As anticipated, this represents a very dramatic reduction in basis size—i.e. down to M = 1,331 or N₈ = 3.138 × 10^{12} (for N = 4). Put another way, such small L values suggest that explicit classical CCS calculations up to N = 6 may be possible.

3.2 Harmonium

The Hamiltonian for the harmonium system is identical to that of the standard electronic structure form of Eq. 8, except that the attractive bare Coulomb external potential is replaced with the
following confining harmonic field $V_{\text{ext}}(x_i, y_i, z_i)$:

$$V_{\text{ext}}(x_i, y_i, z_i) = \frac{\omega^2}{2} \left( x_i^2 + y_i^2 + z_i^2 \right) \quad (14)$$

As a technical matter, too, we consider harmonium with a Yukawa, rather than Coulomb, form for the pair repulsion potential:

$$V_{\text{rep}}(\vec{r}_i, \vec{r}_j) = e^{-\gamma |\vec{r}_i - \vec{r}_j|} \quad (15)$$

One of the remarkable features of harmonium—or the “Hooke atom,” as it is also called—is that (nearly) analytical solutions exist for the $N = 2$ case, despite the coupling implied by the pair repulsion contribution. This makes it possible to compare numerically computed results directly with “exact” values, thus offering an excellent opportunity to benchmark new methods.

For our purposes, we are also interested in harmonium as an “intermediate” test case, lying in between the pathological Coulomb $V_{\text{ext}}$ form of the atomic models, and the $V_{\text{ext}} = 0$ form of the correlated electron gas model (Sec. 3.1). In particular, we expect that the plane-wave basis—though not an especially good choice for harmonium—will nevertheless perform far better here than for bare Coulomb potentials. Of course, there are many contexts in electronic structure in which the bare Coulomb interaction is replaced with “milder” forms—e.g., screened potentials (including SCF), effective core potentials, “softened” Coulomb potentials, etc.

In Ref. [59] we used Andromeda to perform a classical CCS calculation of the 20 lowest-lying energy eigenstates (i.e., energy levels and wavefunctions) for the $N = 2$ harmonium system with $\omega = 1/2$ and $\gamma = 1$ (in atomic units). This parameter choice guarantees “non-trivial” behavior—with neither the external confining field nor the interparticle repulsion contribution dominating. By comparing with the exact analytical results, we were able to confirm an overall numerical convergence of all states to better than $1/2$ millihartree. These values imply a very small basis set truncation error—which, in any event, is likely to be much smaller than other sources of numerical error for this calculation.

| State index | Spatial irrep | Energy | Error |
|-------------|--------------|--------|-------|
| 1           | $A_1$        | 3.6341 | -0.0004 |
| 2           | $A_1$        | 3.9406 | -0.0010 |
| 3           | $A_1$        | 3.9572 | -0.0025 |
| 4           | $A_1$        | 3.9663 | -0.0017 |
| 5           | $T_2$        | 4.1045 | -0.0007 |
| 6           | $T_2$        | 4.1288 | -0.0010 |
| 7           | $T_2$        | 4.1349 | -0.0021 |
| 8           | $A_1$        | 4.3455 | -0.0029 |
| 9           | $A_1$        | 4.3668 | -0.0048 |
| 10          | $A_1$        | 4.4304 | -0.0025 |
| 11          | $A_1$        | 4.4540 | -0.0036 |
| 12          | $A_1$        | 4.4799 | -0.0036 |
| 13          | $T_2$        | 4.4945 | -0.0016 |
| 14          | $T_2$        | 4.4999 | -0.0020 |
| 15          | $T_2$        | 4.5057 | -0.0021 |

4 Results: Quantum Computing Implementation

As discussed, in “first quantized” QCC,[8–15,20–23,25–29] the wavefunction is represented explicitly, as a function over the entire 3N-dimensional configuration space of electron positions. A set of logical qubits is used for this purpose—e.g., to represent the value of the wavefunction at each of a set of uniformly-spaced sinc grid points, forming a 3N-dimensional lattice. An initial wavefunction is generated, and then manipulated through specialized quantum circuitry, in order to simulate the action of the Hamiltonian. Eventually, through many such manipulations, the time-dependent evolution of the initial wavefunction is simulated—or alternatively, the energy eigenstates are computed.

For the types of quantum chemistry applications for which QCC methods can currently be implemented, using today’s quantum (or hybrid quantum/classical) computers, the second-quantized methods have the upper hand. This is because such calculations use the standard simplifying approximations, wherein the number of orbitals, $M$, and/or or the number of SDs, $M/N$, is greatly reduced from the CBS-limit and/or full-CI values. This yields a greatly simplified calculation requiring exponentially less computational effort than a fully converged calculation—which is generally not currently feasible on either classical or quantum computers except for very small systems. As a consequence, the first-quantized methods require more logical qubits, to an extent that is still a bit out of reach, even for simple applications.

On the other hand, the list of such simple applications that have actually been realized using second-quantized QCC—which includes, e.g. crude ground state calculations for the H2 molecule and other two-electron systems,[29–31]—still remains short and unimpressive in comparison with state-of-the-art quantum chemistry on classical computers.[72,73] In the coming years, as quantum computing technology develops and larger QCC applications can be realized, we will reach the point where first-quantized methods overtake second-quantized methods, vis-à-vis their efficiency and accuracy on quantum computers, and their ability
to be run solely on bona fide quantum computers as opposed to hybrid platforms.

As discussed, the primary feature here is that the cost to store the wavefunction, in terms of the required number of logical qubits, scales only linearly with \( N \). Our first task in this section, then, is to estimate the number of logical qubits required. Our second task shall be to explain the quantum circuitry used to implement the above-mentioned Hamiltonian-based manipulations of the wavefunction, in precise detail. This we shall do both for the “standard” or canonical Trotter approach, and also for our alternate CCS-based Trotter implementation, to which the former will be compared.

4.1 Explicit Quantum Representation of the Wavefunction

Note that both tasks above depend intimately on the choice of basis set. For convenience and simplicity, we shall throughout this section presume either a plane-wave, or a sinc (plane-wave dual), basis representation—with the latter related to the former via an inverse Fourier transform. Note that both basis representations conform to Eq. (2). Let \( |\psi\rangle \) denote the \( 3N \)-dimensional numerical wavefunction vector, whose individual components are denoted

\[
|\Psi_{m_1, m_2, m_3}\rangle = |\psi_{m_1, m_2, m_3, \ldots, m_{3N}}\rangle
\]

from Eqs. (2) and (3). There are clearly \( L^{3N} \) such components in all.

The total number of logical qubits needed to represent the entire \( |\psi\rangle \) is thus \( 3Nn \), with \( L = 2^n \). Thus, for \( L \approx 100 \), we can expect \( n \approx 7 \). Note that for each of the \( 3N \) coordinates, \( d_i \), there is a specific set of \( n \) qubits, used to represent the \( L \) corresponding one-dimensional basis functions, \( \phi_{d_i}^{m_1} (x_i) \). We therefore associate each such bundle of \( n \) qubits with the coordinate \( d_i \), but also with the part of the wavefunction associated with that coordinate, which we call \( |\psi_{d_i}\rangle \). Note that the concept of \( |\psi_{d_i}\rangle \) has meaning in quantum computing, even when \( |\psi\rangle \) itself is not separable per se.

In quantum computing circuit diagrams, individual qubits are traditionally represented as horizontal “wires”. These flow from left to right, encountering various quantum gates along the way that alter the qubit states—and thereby, also, the corresponding \( |\psi\rangle \). In addition to the logical qubits representing \( |\psi\rangle \), various “ancilla” or workspace qubits are also often relied upon, to be used at various stages throughout the quantum computation. These are often used to get around unitarity restrictions—although here, the ancilla qubits generally represent function outputs. Ancilla qubits are typically presumed to be in an initial (and often final) state of “zero”, which we denote as \( |0\rangle \).

Some additional quantum circuit conventions that we adopt here are described next. Since for each dimensional set, the number of qubits, \( n \), is fixed—and since there is no reason to consider subdividing below the level of a single coordinate—in all of the quantum circuit diagrams presented here, we treat connections involving \( |\psi_{d_i}\rangle \) as if they were single-qubit wires, rather than bundles. As additional notation, let \( |\psi\rangle \) represent the part of \( |\psi\rangle \) associated with particle \( i \), spanning all three Cartesian coordinates, \( x_i, y_i, \) and \( z_i \). Likewise, \( |\psi_{ij}\rangle \) includes all Cartesian coordinates for particles \( i \) and \( j \), whereas \( |\psi_{jd}\rangle \) includes just the two \( d \)th components—e.g., \( |\psi_{12}\rangle \), associated with \( x_1 \) and \( x_2 \). Also, whereas \( |\psi\rangle \) refers to the wavefunction in the sinc representation, the corresponding Fourier or plane-wave representation is denoted \( |\psi\rangle \). Finally, the usual “slash” notation will be used for ancilla qubit bundles, representing function outputs. To achieve chemical accuracy, each such bundle will typically require around 15–20 qubits.

4.2 Quantum Circuitry: Canonical Trotter Method

Next we address the second task above, i.e. describing the quantum circuitry necessary to implement the requisite Hamiltonian manipulations of \( |\psi\rangle \). For both time-independent and time-dependent QCC applications, one must apply unitary time evolution of the form \( |\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle \), where \( |\psi(0)\rangle \) is the initial wavefunction. In the time-dependent context, this directly propagates the wavefunction, as desired. In the time-independent context, \( \hat{U}(\epsilon) \) is used to obtain the ground eigenstate (and in some cases, excited eigenstates); however, this too requires unitary time evolution of the above form.

The specific form of the time-evolution operator is \( \hat{U}(t) = \exp \left[-i\hat{H}t/\hbar\right] \), where \( t \) is the final time, and \( \hbar \) is the reduced Planck’s constant (taken to be unity in all that follows). In the canonical Trotter method, this is implemented via repeated applications of \( \hat{U}(\epsilon) \), where \( \epsilon \) is a sufficiently small time step such that the individual contributions from Eq. (5) can be treated separately. In other words,

\[
\hat{U}(\epsilon) \approx \cdots \exp \left[-i\hat{V}_{ee}(x_1, y_1, z_1)\right] \times \exp \left[-i\hat{V}_{ex}(x_1, y_1, z_1)\right] \times \cdots \exp \left[-i\hat{\rho}_{1z}^2/2\epsilon\right] \exp \left[-i\hat{\rho}_{1y}^2/2\epsilon\right] \exp \left[-i\hat{\rho}_{1x}^2/2\epsilon\right] ,
\]

an approximation known as "Trotterization," or the Lie-Trotter-Suzuki decomposition. An overview of the quantum circuit implementation of \( \hat{U}(\epsilon)|\psi\rangle \), based on Eq. (17), is presented in Fig. 1. Note that the associated ancilla bits, needed to carry out the individual operations in practice, are not indicated in this figure.

We next turn to the canonical Trotter implementation of the various Hamiltonian component contributions in Eq. (17) and Fig. 1. To begin, we note that it is easiest to implement matrix-vector products on a quantum computer, if the matrix is diagonal. Then, the additional condition of unitarity implies that each \( |\psi\rangle \) component is simply multiplied by some phase shift. However, we further note that, due to basis set truncation error, the sinc basis representation is only an approximate position representation. Thus, in reality, an exact sinc-function representation of the potential energy contributions in Eq. (17) gives rise to matrices that are only nearly diagonal. More specifically, we find that the sinc functions themselves are not true Dirac delta functions, but rather, narrowly peaked functions centered around a uniformly-distributed set of discrete grid points, known as the “sinc discrete variable representation” (sinc DVR) grid points.

We are therefore led to a natural, diagonal, grid-based ap-
proximation to the true potential matrices, obtained by simply evaluating the potential function at the individual sinc DVR grid points, taking these values to comprise the diagonal matrix elements, and then setting the off-diagonal elements to zero.\cite{21} Note that this procedure introduces new "quadrature error," above and beyond the basis set truncation error already present\cite{21 22} Coulombic potentials—being both singular and long-range—present a "worst-case scenario" in terms of sinc DVR quadrature error. For example, one must avoid placing sinc DVR grid points directly on Coulombic singularities, or the sinc DVR matrix elements become infinite! On the other hand, the basis set truncation errors associated with sinc or plane-wave representations of Coulomb potentials also present a worst-case scenario, as discussed previously.

In any event, it is in this fashion that the potential energy contributions in Eq. (17) are implemented—i.e., as phase shifts obtained from potential energy evaluation at the sinc DVR grid points. Put another way, since the potential energy matrices are diagonal in the sinc DVR, their contribution to the time evolution can be implemented using ordinary function evaluation—a standard operation for quantum computers.\cite{21 22 21 22 21 22} Note that each such function evaluation involves only a subset of coordinates—and therefore only a subset of qubits, as indicated in Fig. 1. Specifically, each external (V_{ext}) or pair repulsion (V_{ee}) potential energy term involves three or six coordinates, respectively.

Based on the above description in terms of sinc DVRs, the quantum circuit used to implement \( \exp(-i\varepsilon V_{ee}) |\psi_{12}\rangle \) is given in Fig. 2. A bundle of ancilla qubits (lowest wire) is used to represent the value of the function, \( V_{12} = V_{ee}(x_1, y_1, z_1, x_2, y_2, z_2) \), which becomes the output of the first gate encountered—i.e., the V_{ee} gate indicated near the lower-left corner. Note that this gate also receives input from six explicit coordinates or sets of qubits—i.e., 6n qubits in all, in addition to the ancilla bundle. These act as "control qubits," associated with specific sinc DVR grid points, whose purpose is to determine the associated function output value. Once the latter value is determined, it is then directed to the second gate, where it is used to effect a phase shift. Note that as a matter of notation, we use \( e^{-i\varepsilon V_{12}} \) to refer to the phase shift gate in the quantum circuit diagram, whereas \( \exp(-i\varepsilon V_{ee}) \) refers to the corresponding quantum operator. Finally, a second V_{ee} function evaluation is applied, in order to "reset" the ancilla qubits.

The implementation of the V_{ee} function evaluation gate is complex. Not only does this gate receive input from many control and ancilla qubits, but the standard pair repulsion function itself is also highly correlated, and involves Coulombic singularities that must be carefully avoided. In addition to multiplications and addi-
tions, which are fairly straightforward to implement (even error-corrected) on a quantum computer, the \( V_{ee} \) function also requires evaluation of an inverse square-root, which at present is extremely costly if high accuracy is required. All of this implies a large circuit complexity—rendering the \( \exp(-i\hat{V}_{ee}) \) operation the computational bottleneck of the entire canonical Trotter approach (as indeed, is also generally the case for classical algorithms).

For \( \exp(-i\hat{V}_{ex}) \), a similar, but simpler circuit than Fig. 2 may be used, for which there are only three explicit coordinates and thus three sets of control qubits, associated with a single particle. However, this still represents greater complexity than is desired. As a design goal, we seek to reduce the complexity of the calculation down to a few operations involving no more than one or two qubit sets:

1. operations that involve a change of representation (e.g., QFT) should be efficiently reducible to a single qubit set.
2. operations that do not involve a change of representation should be efficiently reducible to two qubit sets.

It remains to consider the kinetic energy contributions to Eq. (17). From Fig. 1 we observe that each such contribution satisfies Condition 1. above; only a single qubit set is involved. This is, of course, because of the fact that the kinetic energy is separable by both particle and Cartesian component. On the other hand, the \( \hat{p}_{id}^2/(2m_e) \) contributions are decidedly not diagonal in the sinc representation. A Fourier transform is thus required—to transform from the sinc to the plane wave representations, in terms of which the matrix representation of \( \hat{p}_{id}^2/(2m_e) \) becomes diagonal.

This is performed using the standard quantum Fourier transform (QFT) algorithm\cite{111-155} denoted “FT” in the quantum circuit diagrams. Specifically, FT is applied to \( |\psi_{ad}\rangle \), which thus becomes \( |\psi_{id}\rangle \). Then, the \( e^{-i\hat{p}_{id}^2/2m_e} \) phase shift can be implemented, in similar fashion to Fig. 2. The quantum circuit implementation for this entire \( \exp(-i\hat{V}_{ee}) |\psi_{1x}\rangle \) operation is indicated in Fig. 3 for \( i = 1 \) and \( d = x \).

\[
\begin{align*}
|\psi_{1x}\rangle & \quad \text{FT} \\
0 & \quad \text{exp}\left(-i\frac{\hat{p}_{id}^2}{2m_e}\right) \\
\text{FT}^\dagger & \quad \exp\left(-i\frac{\hat{p}_{id}^2}{2m_e}\right)
\end{align*}
\]

Fig. 3 Quantum circuit to implement \( \exp(-i\hat{V}_{ee}) |\psi_{1x}\rangle \) on a quantum computer. The function evaluation involves just a single coordinate (the momentum \( p_{1x} \)), and hence just a single qubit set. This circuit is used in both the canonical and CCS Trotter quantum circuitry.

### 4.3 Quantum Circuitry: CCS Trotter Method

For the CCS implementation proposed here, much of the canonical Trotter quantum circuitry can be retained. In particular, from a high-level perspective, the overview as presented in Fig. 1 applies equally well to both the canonical and CCS Trotter quantum strategies. Our CCS implementation as presented here is thus also a Trotterized approach. Furthermore, action of the kinetic energy operator is still implemented exactly as in Fig. 3 as it adheres to our “design philosophy” as described in Sec. 4.2.

On the other hand, the CCS implementations for \( \exp(-i\hat{V}_{ex}) \), and for the bottleneck \( \exp(-i\hat{V}_{ee}) \) operation, are very different from the canonical approach. Specifically, we pursue a quantum circuit implementation in keeping with the CCS tensor-SOP decomposition described in Sec. 2.3. For brevity, we focus the discussion that follows on the more challenging case of implementing \( \exp(-i\hat{V}_{ee}) \), although similar procedures can also be applied for \( \exp(-i\hat{V}_{ex}) \).

From the CCS tensor-SOP form of Eq. (9), it is clear that a natural quantum circuit implementation for \( \exp(-i\hat{V}_{ee}) |\psi_{12}\rangle \) should take the form presented in Fig. 4. In comparing with the canonical quantum circuit of Fig. 2 we see that the two implementations are completely different. The CCS version would appear to offer many advantages. In particular, the six-dimensional function calls are replaced with \( \exp(-i\hat{p}^2_{id}/2m_e) |\psi_{12}\rangle \) operations involving just two coordinates (e.g. \( x_1 \) and \( x_2 \))—thereby satisfying design Condition 2. above. Moreover, the \( \hat{p}^2_{id} \) functions themselves are Gaussians, with very smooth behavior and a restricted, well-defined range.

\[
\begin{align*}
|\psi_{12}\rangle & \quad \text{FT} \\
0 & \quad \text{exp}\left(-i\frac{\hat{p}_{id}^2}{2m_e}\right) \\
\text{FT}^\dagger & \quad \exp\left(-i\frac{\hat{p}_{id}^2}{2m_e}\right)
\end{align*}
\]

Fig. 4 CCS quantum circuit to implement \( \exp(-i\hat{V}_{ee}) |\psi_{12}\rangle \) on a quantum computer, based on Eq. (9). The six-dimensional \( V_{ee} \) function gate of Fig. 2 is now replaced with two-dimensional function gates, which separate by Cartesian component. The two-particle wavefunction contribution \( |\psi_{12}\rangle \) decomposes naturally into \( |\psi_{12x}\rangle, |\psi_{12y}\rangle \), and \( |\psi_{12z}\rangle \) components.

As implied above, the \( \hat{p}^2_{id} \) matrix representations are diagonal in the sinc DVR, and thus amenable to a straightforward quantum circuit implementation—i.e., essentially a two-dimensional version of Fig. 2. The specific quantum circuit used to implement \( \exp(-i\hat{p}^2_{id}/2m_e) |\psi_{12}\rangle \) in the sinc DVR is presented in Fig. 5. Note that a similar quantum circuit may be employed for the CCS tensor-SOP components of \( V_{ext} \), except that only a single coordinate or set of control qubits is needed.

Diagonal sinc DVR \( \hat{p}^2_{id} \) matrices certainly present one reasonable avenue for QCC implementation of the CCS approach. Their Gaussian form, moreover, implies that far fewer grid points would be needed to represent \( \hat{V}_{ee} \) than in the canonical approach (to the same level of accuracy). On the other hand, a sinc DVR calculation still does introduce some quadrature error, which does not exist in the classical CCS implementation—e.g., as was used to generate the results of Sec. 3. For this reason, it might be less efficient, in terms of basis size, than the corresponding classical
Fig. 5 CCS quantum circuit to implement \( \exp(-i \beta^2 \gamma |x_1 - x_2|^2) \) on a quantum computer, in the sinc DVR. The function evaluation, 
\( \gamma^1 = \exp(-\beta_1^2 (x_1 - x_2)^2) \), involves two explicit coordinates and sets of qubits, and includes an exponential function evaluation.

Calculation. That said, insofar as factors determining the necessary basis size is concerned, \( V_{\text{ex}} \) is much more important than \( V_{\text{nc}} \), if bare Coulomb potentials are used. Consequently, it is not so clear how much worse this CCS form of quadrature error would actually make things, in practice.

Nevertheless, we maintain that it is worth the effort to try to develop alternate QCC implementations that use exact sinc \( \gamma^3 \) matrices (i.e., as computed without recourse to sinc DVR grid points)—thereby eliminating all quadrature error, and reducing the basis size still further, down to exactly the number used in classical calculations. In this context, the greatest challenge is posed by the fact that the exact matrices are no longer diagonal. Also, though still quite small by virtue of being two-dimensional, they are not quite small enough to satisfy our design conditions.

Despite the above challenges, we have developed an exact sinc QCC implementation that not only overcomes the non-diagonal limitation, but also satisfies both design conditions. This approach is based on the fact that the off-diagonal part of an exact \( \gamma \) matrix can be written in the form \( \hat{\gamma}_{\text{offdiag}} = (\hat{\rho}_1 \hat{D} + \hat{\rho}_2 \hat{D})/2 \) —where \( \hat{D} \) is diagonal, and \( \hat{\rho} \) subscripts (and \( \gamma \) superscripts) have been dropped for clarity. In the \( \epsilon \to 0 \) limit, Trotterization then yields

\[
\exp(-i \epsilon \hat{\gamma}_{\text{offdiag}}) \approx \exp(-i \epsilon \hat{\rho}_1 \hat{D}/2) \exp(-i \epsilon \hat{\rho}_2 \hat{D}/2).
\]  

Note that the individual factors in Eq. \((15)\) above are no longer unitary; the exponents are comprised of non-commutative operator—rather than tensor—products. Although some algorithms have come on the scene very recently \cite{92,93}, we have developed our own QCC implementation that is unitary, and correct to first order in \( \epsilon \). It involves separate \( FT \) operators for \( \hat{\rho}_1 \) and \( \hat{\rho}_2 \), and also a two-dimensional function evaluation for \( \hat{D} \)—thereby satisfying our two design conditions. As this work is currently under review by Texas Tech University for possible patent protection, further details will be presented in a future publication.

5 Conclusions

The frontier in quantum chemistry calculations has always involved pushing the following limits: (a) full CI; (b) complete basis set (CBS); (c) number of explicit electrons, \( N \). All of these imply a substantial increase in \( N_B \), the basis size or number of Slater Determinants (SDs) needed to perform the calculation. Over the decades—but especially in the last 10 years or so—impressive and steady progress has been made towards increasing the number of SDs that can be treated explicitly in calculations \cite{4,7,2,5,1,5,92,93}

Much of the recent progress has relied on massive parallelization, but use of tensor decompositions of various kinds is also playing an increasingly important role. Moreover, going forward, it is clear that quantum computing—for which exponential growth in \( N_B \) corresponds to mere linear growth in the number of logical qubits—will engender an even greater sea change. This long-awaited “quantum computational chemistry (QCC) revolution” \cite{43,35} may be nearly upon us, although achieving full quantum supremacy will likely have to wait for quantum platforms that can accommodate first-quantized methods.

Whatever the future may bring, it seems that the quantum chemistry discipline may be at a “tipping point”—a nexus, where there is once again room to consider bold new ideas. One such idea—that the electronic structure Hamiltonian operator separates more naturally by Cartesian component than by particle—represents a radical departure from the traditional particle-separation starting point, and serves as the focus of this work. In addition to directly addressing the traditional three limits, (a)–(c) above, the CCS approach also has ramifications for two additional quantum chemistry frontiers: (d) calculation of many excited states (including wavefunctions); (e) application to combined electron-nuclear motion quantum many-body problem. These latter two require \( N_B \times N_B \) matrix diagonalization (as opposed to just calculation of the ground state), as well as the ability to go beyond traditional SD representations. Frontier (e) is, in addition, of special relevance for QCC.

In this study, we have sought to demonstrate the potential advantages presented by the CCS approach in both classical and quantum computing contexts. On the classical side, the CCS tensor-SOP decomposition of the wavefunction (Eq. \((3)\) enables astronomical basis sizes to be considered with minimal RAM requirements—e.g., \( N_B \approx 10^{15} \) for the harmonic calculation performed in the present work, and up to \( N_B \approx 10^{16} \) more generally. Of even greater import is the CCS tensor-SOP decomposition of the Hamiltonian operator itself, which reduces the complexity of both the classical and quantum calculations—essentially by restricting the set of coordinates that must be considered at one time, from six down to two.

It is worth discussing the quantum or CCS QCC case a bit further. In Sec. 4.3 we have presented two different CCS Trotter implementations—i.e., the exact non-diagonal sinc option, and the approximate diagonal sinc-DVR option. Both of these represent an improvement over the standard canonical Trotter QCC implementation, in that: (i) only two coordinates need be dealt with at a time (potentially implying fewer quantum gates), and; (ii) quadrature error is reduced or eliminated entirely (implying fewer basis functions or qubits). In comparing the two CCS QCC implementations to each other, however, we find that the exact non-diagonal implementation requires more quantum gates, but fewer qubits, than the diagonal sinc-DVR alternative—thereby
presenting a useful “engineering tradeoff.” On the other hand, the computational bottleneck in either case is likely to be evaluation of the Gaussian or exponential function—which, like the inverse square-root, is also currently very expensive on quantum computers. Indeed, this cost could be so great as to render the various potential advantages of the CCS approach (e.g., the reduction in circuit complexity that might otherwise occur) largely moot, in practice.

In a companion paper, we will present a new algorithm for evaluating Gaussian and exponential functions efficiently on quantum computers. The cost is the same as that of performing a fairly small number of multiplications (with or without error correction) and is thus on a par with the other costs associated with the present CCS QCC algorithm. Running together with the new exponentiation algorithm, then, the present approach would appear to become a highly competitive contender for first-quantized QCC.

We conclude by once again stressing the key point that the full benefits of the CCS approach have yet to be realized. This is because to date, all calculations have been performed using plane-wave and/or sinc basis functions, which represent a terrible choice for Coulomb systems. As discussed, something like \(L \approx 100\) is required for such systems, corresponding to \(M = L^3 = 10^6\) single-particle orbitals. For harmonium, plane waves are a reasonably good—but still not great—choice of basis. Here, we find a reduction to \(L = 17\) or \(M \approx 5000\). For the uniform or correlated electron gas application, plane waves are of course a much better choice, giving rise to \(L = 11\), or \(M \approx 1000\) orbitals. All of these are requirements for achieving chemical accuracy.

The main lesson here is the unsurprising one that a suitable choice of CCS basis for a given application can lead to a dramatic reduction in basis size. Ultimately, this should result in explicit classical calculations up to perhaps \(N = 6\). Larger calculations could also be performed, using the output of a CCS calculation as a highly-efficient, multi-particle basis set (i.e., the \(N\)-particle, CCS version of a geminal basis set). Of course in practice, this will first require the development of the “optimal CCS basis” (OCCSB) functions of the Eq. (1) form—i.e., the CCS analog of HF molecular orbitals.

As a technical matter, we advocate use of optimal separable basis theory to compute the OCCSB functions (rather than traditional SCF), because the result is an optimized, complete orthonormal basis obtained “all at once” (as opposed to a collection of non-orthogonal ground and excited state SCF functions obtained one at a time). In any event, and as mentioned several times, the individual OCCSB functions will incorporate correlation implicitly—thus potentially dramatically reducing the required basis size, even in cases where electron correlation is severe. At the same time, the CCS tensor decomposition enables classical computers to handle \(N_b = 10^{15}\) or more basis functions, which is very promising.

Of course, OCCSB calculations have yet to be performed on classical computers, the era of first-quantized QCC is still a ways off, and it is never certain what the future will bring. Nevertheless, one thing already seems quite clear: it is best to have a variety of different methods in one’s computational arsenal— as indeed, has been the case within the confines of traditional second-quantized classical quantum chemistry for decades.

**Conflicts of interest**

There are no conflicts to declare.

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