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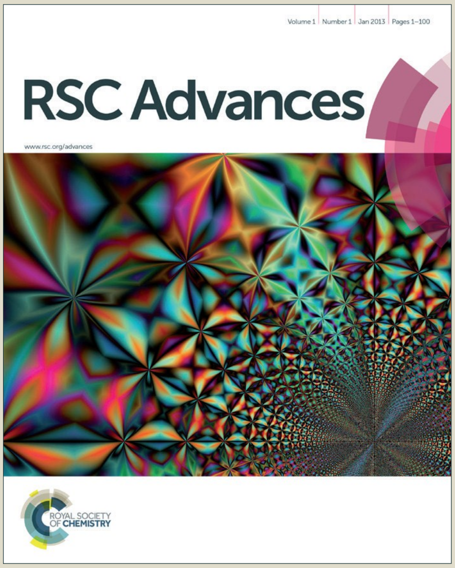

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Compact wavefunctions from compressed imaginary time evolution

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Conspectus

Simulation of quantum systems promises to deliver physical and chemical predictions for the frontiers of technology. In this work, we introduce a general and efficient black box method for many-body quantum systems using technology from compressed sensing to find compact wavefunctions without detailed knowledge of the system. No knowledge is assumed in the structure of the problem other than correct particle statistics. As an application, we use this technique to compute ground state electronic wavefunctions of hydrogen fluoride and recover 98% of the basis set correlation energy or equivalently 99.996% of the total energy with 50 configurations out of a possible 10^7.

Introduction - The prediction of chemical, physical, and material properties from first principles has long been the goal of computational scientists. The Schrödinger equation contains the required information for this task, however its exact solution remains intractable for all but the smallest systems, due to the exponentially growing space in which the solutions exist. To make progress in prediction, many approximate schemes have been developed over

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*To whom correspondence should be addressed the years that treat the problem in some small part of this exponential space. Some of the more popular methods in both chemistry and physics include Hartree-Fock, approximate density functional theory, valence bond theory, perturbation theory, coupled cluster methods, multi-configurational methods, and more recently density matrix renormalization group.[1–10]

These methods have been successful in a wide array of problems due largely to the intricate physics they compactly encode. For example, methods which are essentially exact and scale only polynomially with the size of the system have been developed for one-dimensional gapped quantum systems.[11] However such structure is not always easy to identify or even present as the size and complexity of the systems grow. For example, some biologically important transition metal compounds as well as metal clusters lack obvious structure, and remain intractable with current methods.[12–14]

The field of compressed sensing exploits a general type of structure, namely simplicity or sparsity, which has been empirically observed and is adaptive to the problem at hand. Recent developments in compressed sensing have revived the notion that Occam's razor is at work in physical systems. That is, the simplest feasible solution is often the correct one. Compressed sensing techniques have had success in quantum simulation in the context of localized wavefunctions[15] and vibrational dynamics of quantum systems,[16,17] but little has been done to exploit the possibilities for many-body eigenstates, which are critically important in the analysis and study of physical systems. Much work has been done on finding sparse representations of orthogonal CI wavefuntions, with early work utilizing perturbative selection by Harrison[18] and stochastic selection by Greer and Zhang.[19,20] Moreover, we note that while this work was under review, a paper by Knowles appeared applying a penalty function compressive sampling approach to orthogonal CI wavefunctions[21] and work by Olsen appeared highlighting the power of non-orthogonal CI wavefunctions in hard problems such as the Chromium dimer.[22] While our approach differs from these two works, they highlight the importance of two foundational aspects, namely sparsity and flexibility in the wavefunction ansatz.

In this letter, we concisely describe a new methodology for finding compact ground state eigenfunctions for quantum systems. It is a Multicomponent Adaptive Greedy Iterative Compression (MAGIC) scheme. This method is general in that it is not restricted to a specific ansatz or type of quantum system. It operates by expanding the wavefunction with imaginary time evolution, while greedily compressing it with orthogonal matching pursuit.[23] Matching pursuit and its variants are greedy algorithms in the standard sense, that is, at each step they select a new optimal component without regard to the consequences this may have on future steps. As an example application, we choose the simplest possible ansatze for quantum chemistry, sums of non-orthogonal determinants, and demonstrate that extremely accurate solutions are possible with very compact wavefunctions. This non-orthogonal MAGIC scheme we refer to as NOMAGIC, and apply it to electronic wavefunctions in quantum chemistry.

Compressed imaginary time evolution - Beginning with general quantum systems, an N-particle eigenfunction of a quantum Hamiltonian H, $|\Psi\rangle$, may be approximated by a trial function $|\tilde{\Psi}\rangle$ that is the sum of many-particle component functions $|\Phi^i\rangle$, such that

$$|\tilde{\Psi}\rangle = \sum_i^{N_c} c_i \, |\Phi^i\rangle \tag{1}$$

where N_c is the total number of configurations in the sum and no relation need be assumed between $|\Phi^i\rangle$ and $|\Phi^j\rangle$ for $i \neq j$. A simple example of such a component function for a general quantum system is the tensor product of N single particle functions $|\phi_j^i\rangle$

$$|\Phi^i\rangle = |\phi_0^i\rangle \, |\phi_1^i\rangle \, ... \, |\phi_{N-1}^i\rangle \tag{2}$$

and we will consider its anti-symmetric counterpart in applications to electronic systems. In this work, we define a state to be simple, sparse, or compact if the number of configurations, N_c, required to represent a state is much smaller than the total dimension of the Hilbert space. Note that in order for this definition to be meaningful, one must restrict the possible transformations of the basis. If arbitrary basis transformations are allowed, the complexity of the state may be hidden in the transformation to allow a trivial state representation. As such, we consider the sparsity of the state as given and under all invertible single-particle basis transformations that conserve essential symmetries. These transformations are known to rigorously preserve the number of configurations N_c.[24]

One method for determining $|\tilde{\Psi}\rangle$ is a direct variational approach based on the particular parametrization of $|\Phi^i\rangle$ and choice of N_c. This approach can be plagued by issues related to the choice of initial states, difficulty of adding new states, and numerical instability of the optimization procedure if proper regularization is not applied.[24–28]

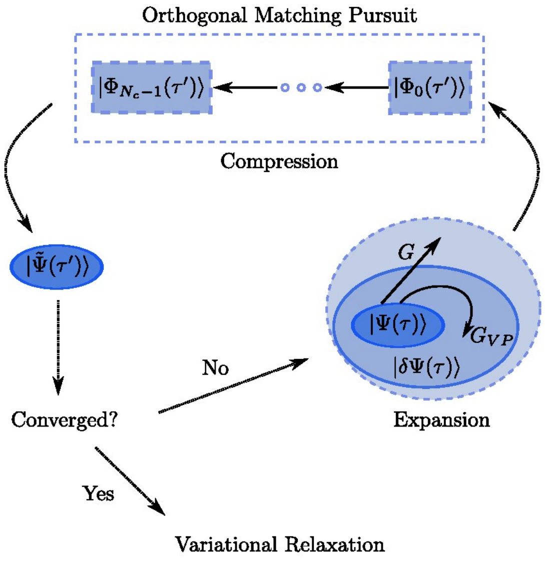

Figure 1: A schematic diagram of the MAGIC approach. At each iteration the wavefunction is expanded by means of the imaginary time propagator G, and subsequently compressed with orthogonal matching pursuit. The imaginary time propagator corresponding to projection into the manifold at $|\Psi(\tau)\rangle$, denoted $|\delta\Psi(\tau)\rangle$, typically prescribed by differential time dependent variational principles is given as G_{VP} and depicted to emphasize that expansion with the operator G can explore a greater part of Hilbert space. The compression is performed simultaneously with expansion in our implementation to prevent rapid growth of the wavefunction. These steps are iterated until convergence at a specified maximum number of component functions, at which point an optional variational relaxation may be performed.

We present an alternative technique that selects the important configurations in a black-box manner and is naturally regularized to prevent numerical instability. By black-box here, we mean only that no expert user input is used in the method once a physical system has been selected. The wavefunction is built automatically through a combination of imaginary-time evolution and compressed sensing. Imaginary-time evolution can be concisely described as follows. Given a quantum system with a time-independent Hamiltonian H and associated eigenvectors $\{|\chi^i\rangle\}$, any state of the system $|\Omega\rangle$ may be expressed in terms of those eigenvectors as

$$|\Omega\rangle = \sum_i c_i |\chi^i\rangle \tag{3}$$

and the the evolution of the system for imaginary-time τ is given as

$$G|\Omega\rangle = e^{-H\tau}|\Omega\rangle = \sum_i c_i e^{-E_i \tau} |\chi^i\rangle \tag{4}$$

where $E_0 < E_1 \leq E_2 ... \leq E_{N-1}$ are the eigenenergies associated with $|\chi_i\rangle$. By evolving and normalizing the wavefunction, eventually one is left with only the eigenvector associated with the lowest eigenvalue, or ground state. Excited states may be obtained with a number of approaches including spectral transformations (e.g. $H' = (H - \lambda)^2$ [29]), matrix deflation, or other techniques. However we will concern ourselves only with ground states in this work.

Imaginary time evolution approaches may be broadly grouped into two classes. The first class involves the explicit application of the imaginary-time propagator G to the wavefunction. This approach typically generates many configurations at every step, causing a rapid expansion in the size of the wavefunction. As a result, these methods have almost exclusively been restricted to Monte Carlo sampling procedures which attempt to assuage this explosion by stochastically sampling or selecting the most important configurations,[30,31] however the recently developed imaginary time-evolving block decimation also belongs to this class, performing truncations after expansion along a virtual bond dimension.[32–35] The Path-Integral renormalization group method also uses this approach to stochastically add non-orthogonal CI determinants, and has been applied to chemical systems such as H_2.[36,37]

Our method differs from this approach in the manner in which new determinants are fit, and the performance benefits of our method can be inferred from the data on H_2 in the appendix of this work.

The second class of imaginary-time approaches follow the evolution dictated by the action of G projected onto the manifold spanned by linear variations in the function at the previous time step, sometimes referred to as Galerkin or time-dependent variational methods including imaginary time MCTDH[38,39] and DMRG in some limits.[35] While computationally convenient, it is often unclear how projection onto the original linear subspace at every time can affect evolution as compared to the exact evolution. In this work, we show that the first class of explicit evolution can be used on any ansatz without configuration explosions or stochastic sampling by utilizing a technique from the field of compressed sensing, namely orthogonal matching pursuit.[23,40]

The algorithm we use is diagrammed in Fig 1, and proceeds iteratively as follows. The wavefunction at time $\tau = 0$, $|\Psi(\tau)\rangle$, may be any trial wavefunction that is not orthogonal to the desired eigenstate. We determine the wavefunction at time $\tau + d\tau = \tau'$ greedily, fitting one configuration $|\Phi^i(\tau')\rangle$ at a time by maximizing the functional

$$\frac{\left| \langle \Phi^i(\tau') | \, G \, |\Psi(\tau)\rangle - \sum_{j<i} c_j(\tau') \langle \Phi^i(\tau') | \Phi^j(\tau') \rangle \right|}{\sqrt{\langle \Phi^i(\tau') | \Phi^i(\tau') \rangle}} \tag{5}$$

with respect to the parameters that determine $|\Phi^i(\tau')\rangle$. Such that after k iterations, the wavefunction is given by

$$|\tilde{\Psi}(\tau)\rangle = \sum_i^k c_i(\tau) \, |\Phi^i(\tau)\rangle \tag{6}$$

The coefficients in this expansion, $c_i(\tau')$ are solved for simultaneously after each iteration by orthogonal projection, which after simplification reduces to the following linear system for the coefficient vector c

$$Sc = v \tag{7}$$

where $S_{ij} = \langle \Phi^i(\tau') | \Phi^j(\tau') \rangle$ and $v_i = \langle \Phi^i(\tau') | G | \Psi(\tau) \rangle$. Together, the fit and orthogonal projection step is equivalent to orthogonal matching pursuit[23,40] applied to the signal generated by the imaginary time evolution of the state at each time step $G |\Psi(\tau)\rangle$. The expansion-compression procedure is advanced to the next imaginary time step either when some accuracy convergence criteria is met, or when some pre-set maximum number of components N_c is reached, and the total simulation is terminated when the wavefunction converges between imaginary-time steps. We provide additional details of the numerical procedure in the supporting information for interested readers.

Note that one is free to choose a convenient form for the propagator G. In this work we use the linearized propagator $G \approx (I - d\tau(H - \lambda))$, which is both easy to implement and provably free of bias in the final result for finite single particle basis sets given some restrictions on $d\tau$.[41] The constant shift λ can be adjusted and is taken to be the expectation value of the energy of the previous imaginary time step in our implementation.

Orthogonal matching pursuit attempts to find the sparsest solution to the problem of state reconstruction,[23,42] and thus is ideal for keeping the number of configurations minimal throughout the imaginary time evolution. However, while the solution is sparsest in the limit of total reconstruction and naturally regularized against configuration collinearity, for very severe truncations of the wavefunction, the sparsifying conditions generate a solution which is not variationally optimal for the given number of configurations. For this reason, we finish the computation with a total variational relaxation of the expectation value of the energy with respect to both coefficients and states that preserves the sparsity in configuration space. This retains both the benefits of imaginary time evolution in avoiding local energetic minima and of variational optimality in the final solution. Note that for finite truncations of imaginary time evolution procedures, some local minima may still be expected, but in practice, the authors have observed that it is far less prevalent than in purely variational methods.

Application to electronic systems - The method we have outlined may be readily applied to any quantum system, such as spins or oscillators, however as a first application we consider ground-state electronic wavefunctions of molecules. We will take the approach that is conventional to the field of quantum chemistry, and solve the problem in a basis of Gaussian-type functions.[8] After a basis has been selected, there is a standard procedure of expanding the linear state space by excitation known as configuration interaction (CI), which can eventually yield the numerically exact solution within a basis when the full state space has been covered. This is referred to as full configuration interaction (FCI) and is the standard to which we compare. Moreover, we compare to truncated orthogonal CI methods that represent a high level of accuracy while yielding an explicit wavefunctions and requiring no additional machinery to evaluate the energy efficiently.[8,43] Comparison to methods considering explicit correlation beyond that covered by a specific traditional Gaussian basis, such as explicitly correlated f_{12} type wavefunctions, are not yet within the scope of this work.

In the context of our approach, the indistinguishability of electrons necessitates handling of anti-symmetry. The simplest way to include anti-symmetry into the wavefunction is by utilizing anti-symmetric component tensors $|\Phi^i\rangle$. The simplest anti-symmetric component function is the Slater determinant, such that we express the wavefunction as

$$|\Psi\rangle = \sum_i^{N_c} c_i \, \mathcal{A}\left(|\phi_0^i\rangle \, |\phi_1^i\rangle \ldots |\phi_{N-1}^i\rangle\right) \equiv \sum_i^{N_c} c_i \, |\Phi^i\rangle \tag{8}$$

where $\mathcal{A}$ is the anti-symmetrization operator and $|\Phi^i\rangle$ are now Slater determinants with no fixed relations between $|\Phi^i\rangle$ and $|\Phi^j\rangle$ for $i \neq j$. While this simple form lacks extensivity,[44] it is attractive for other reasons. Namely the quality of description and rate of convergence

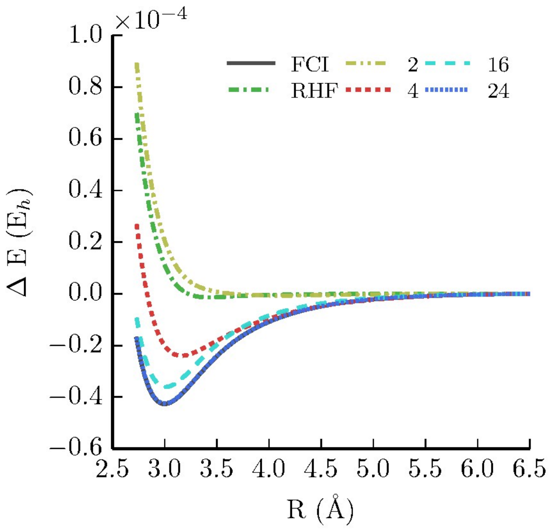

Figure 2: The bond dissociation curve of the helium dimer in the aug-cc-pVDZ basis showing rapid and consistent convergence in the number of non-orthogonal determinants. These represent the nuclear union curves constructed from a number of local determinants at each nuclear point given by the line label, and are sampled at a spacing of 0.04 Å. The curves have been shifted by the tail values in order to allow comparison of the features for this sensitive bond, and the 24 determinant curve is indistinguishable from the FCI solution in the graphic. At a point near the equilibrium geometry, $R = 3.01$ Å, the 24 determinant curve with the nuclear union configuration interaction technique recovers 99.9899% of the basis set correlation energy, or equivalently 99.9999% of the total energy.

in N_c are invariant to invertible local transformations of the state (i.e. atomic orbitals vs. natural orbitals),[24] and the mathematical machinery related to the use and extension of such a wavefunction is already well developed[45–48]

While the method we use for determinant selection is unique, non-orthogonal Slater determinants have been used successfully in valence bond theory[4,5] as well as more recent symmetry breaking and projection methods.[49,50] Unconstrained non-orthogonal Slater determinants have been utilized before, but in a purely variational context.[25,28] Using this machinery yields explicit gradients that we utilize in the optimization of determinants.[48] The scaling of these constructions with current algorithms is $O({N_c}^2 \max(M^2, N_e^3))$[44] where N_c is the number of determinants and N_e is the number of electrons, however development of approximations in this area have received comparatively less attention as compared to orthogonal reference wavefunction methods and there may be ways to improve upon this

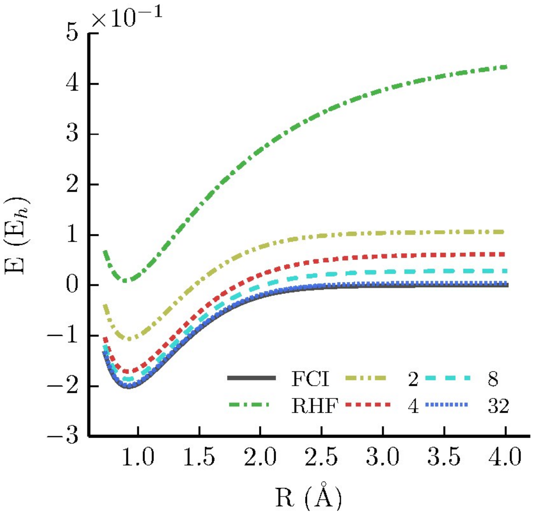

Figure 3: The bond dissociation curve of hydrogen fluoride in the cc-pVDZ basis showing rapid convergence in the number of non-orthogonal determinants. These are the nuclear union curves constructed from a number of local determinants at each nuclear point given by the line label, and are sampled at a spacing of 0.04 Å. The 32 determinant curve is nearly indistinguishable from the FCI curve in this graphic. At a point near the equilibrium geometry, $R = 0.93$ Å, the 32 determinant curve with the nuclear union configuration interaction technique recovers 98.6% of the basis set correlation energy, or equivalently 99.997% of the total energy.

scaling.

We introduce an additional enhancement for the study of chemical reactions that is greatly facilitated by the compactness of our expansions. Namely, when considering a full reaction coordinate, such as that for a bond dissociation, we perform an additional linear variational calculation in the space of components (determinants) found locally at neighbouring nuclear configurations. As a proof of principle, we include configurations from the entire curves in the following examples, but more economical truncations can be used as well. We refer to this additional step, as the nuclear union configuration interaction method and describe it in more depth in the supplemental information.

As a first application, we consider He_2 in the aug-cc-pVDZ basis,[51] which is a standard atom-centered Gaussian quantum chemical basis with additional diffuse functions to better capture the weak dispersive interactions present in rare gas interactions. The helium dimer is unbound in the case of a single determinant with restricted Hartree Fock (RHF) and is

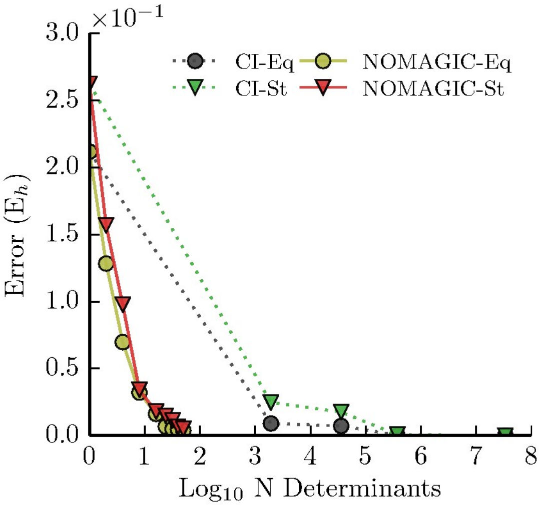

Figure 4: A curve of the energetic error as compared to full CI for HF bond dissociation in the cc-pVDZ basis as a function of the log of the number of determinants included for both a near-equilibrium geometry "Eq" with $R = 0.93$ Å and a stretched geometry "St" with $R = 1.73$ Å. The configuration interaction energies are generated by a standard excitation sequence from the Hartree-Fock solution, CIX(X=SD, SDT, SDTQ) followed by FCI. The number of determinants used in the full CI expansion is approximately 34 million taking into account molecular point group symmetries, or 135 million without. No symmetries other than spin are utilized in the NOMAGIC calculation.

not held together by a covalent bond, but rather dispersive forces and dynamical correlation only. In Fig. 2, we consider the dissociation of this molecule under different numbers of non-orthogonal determinants. Despite the sensitive nature of this bond, it is qualitatively captured with as few as 4 local determinants and quantitatively captured with as few as 24 determinants. The dimension of the space of this molecule is on the order of 10^4 when reduced by considerations of point group symmetry. The NOMAGIC approach does not yet utilize any symmetry other than the spin symmetry enforced by the parameterization of the wavefunction.

As a second example, the dissociation of hydrogen fluoride in a cc-pVDZ basis[52] is studied. The total configuration space for this molecule is on the order of 10^7 and it involves a homolytic bond breaking of a covalent bond in the gas phase. Considering the results in Fig. 3, one can see that while RHF yields an unphysical dissociation solution, as few as 2 determinants are sufficient to fix the solution in a qualitative sense. Beyond this, the addition of more determinants represents a monotonically increasing degree of accuracy, with rapid convergence to a quantitative approximation by 32 determinants.

In Fig. 4 we select two points on the HF dissociation curve, and study the convergence of the energy as a function of the number of determinants in the NOMAGIC method and a traditional CI expansion with the canonical Hartree-Fock orbitals. In particular, we study both a point near the equilibrium bond length ($R = 0.93$ Å) where traditional CI expansions perform relatively well and a more stretched geometry ($R = 1.73$ Å) where traditional CI expansions perform more poorly. We see that in both cases, if one considers a fixed level of accuracy in the energy, the NOMAGIC method is considerably more compact. For example, to achieve a level of accuracy superior to the CISDT expansion that uses 36021 determinants, NOMAGIC requires only 24 determinants at both geometries. That is, for equivalent accuracy, the NOMAGIC wavefunction is roughly 1500 times more compact in the space of Slater determinants. By 50 determinants out of a possible 10^7 in the NOMAGIC wavefunction, we recover 98% of the basis set correlation energy or equivalently 99.996% of the total energy. To further quantify the advantage of computationally for manipulating and evaluating expectations values on compact NOMAGIC states, consider the cost of evaluating the energy of a stored CISDT state and a NOMAGIC state with N_c determinants. A NOMAGIC state with N_c determinants requires $O(N_c^2 \max(M^2, N_e^3))$ operations to evaluate the energy. In contrast, a CISDT state requires $O(M^8)$ operations in the standard case that the number of basis functions M is on the same order as the number of electrons N_e. Thus assuming $N_e \sim M$ there is a clear computational advantage in any case where $N_c < O(M^{5/2})$ provides a sufficiently accurate representation, as has been observed in all examples thus far.

Conclusions - In this work, we introduced a general method to find compact representations of quantum eigenfunctions by using imaginary-time evolution and compression. The method assumes no specific structure in the problem, and thus there are minimal restrictions on the quantum system or ansatze with which it can be attempted. The compact wavefunctions that result from this methodology not only offer potential practical advantages in terms of storage and subsequent evaluation of physical observables, but can also provide a numerical upper-bound on the minimal information necessary to identify a physical quantum state, or Kolmogorov complexity of the state. A low Kolmogorov complexity of physical quantum states would have important ramifications for the growing belief that physical states occupy a small physical "corner of Hilbert space".[53–55] We demonstrated the method's practical success in some quantum chemical systems with a small number of non-orthogonal Slater determinants. One practical application of this method is the creation of extremely compact trial wavefunctions for quantum Monte Carlo, which suffer little additional overhead with the use of non-orthogonal determinants and are often limited by the size of the trial wavefunction.[56,57] Finally, we believe that extensions to this method using ansatze that contain system specific physics have the potential to be even more compact and this is subject of current research.

1 Biographies

Jarrod R. McClean is a Department of Energy Computational Graduate Science Fellow currently studying with Alán Aspuru-Guzik as a PhD student at Harvard University. He is interested in the intersection between traditional and quantum computation for applications to chemistry.

Alán Aspuru-Guzik is Professor of Chemistry and Chemical Biology of Harvard University. His research group works at the intersection of quantum information and chemistry. He has been working on quantum computing for quantum chemistry since 2005. He has received numerous awards including a Technology Review 35 Innovators under 35 award. http://aspuru.chem.harvard.edu

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