Solving the Schrödinger Equation in the Configuration Space with Generative Machine Learning

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Abstract

The configuration interaction approach provides a conceptually simple and powerful approach to solve the Schrödinger equation for realistic molecules and materials but is characterized by an unfavourable scaling, which strongly limits its practical applicability. Effectively selecting only the configurations that actually contribute to the wavefunction is a fundamental step towards practical applications. We propose a machine learning approach that iteratively trains a generative model to preferentially generate the important configurations. By considering molecular applications it is shown that convergence to chemical accuracy can be achieved much more rapidly with respect to random sampling or the Monte Carlo configuration interaction method. This work paves the way to a broader use of generative models to solve the electronic structure problem.

Introduction

The application of machine learning (ML) to quantum chemistry and computational materials science has experienced an impressive growth in the past few years. However, methods

that apply ML to molecular dynamics[1,2] or molecular property predictions[3,4] usually imply the availability of a certain amount of data previously produced by approximating the solution of the Schrödinger equation. By considering the exponential numerical complexity involved in the exact solution of this equation it would be highly desirable to take advantage of ML techniques also in this context. For realistic molecules and materials this is a widely open field of research and the full potential of ML has yet to be widely exploited in its full potential.

In a seminal work Carleo and Troyer showed that neural networks can effectively represent the quantum states of spin models, thus reducing the exponential complexity of the many-body problem.[5] Specifically, they showed that a restricted Boltzmann machine (RBM) used as an ansatz within variational Monte Carlo can achieve variational energies lower than those obtained with traditional approaches. From a theoretical point of view this success relies on universal approximation theorems,[6,7] which imply that neural networks can approximate complex (but "reasonably" smooth) high-dimensional functions, including quantum states. This method was demonstrated numerically considering the one- and two-dimensional Ising and Heisenberg models. More recently Carleo and coworkers have applied a similar approach to realistic Hamiltonians of small molecules.[8] This was achieved by mapping the electronic structure Hamiltonian into a spin-like Hamiltonian by using quantum information encodings. The most accurate results where obtained with the Jordan-Wigner mapping,[9] which leads to an approach equivalent to the configuration interaction (CI).[10] Within the CI method the fully interacting wavefunction is expressed as a linear combination of excited Slater determinants (the "configurations"); while the coefficients of this expansion are typically computed as solution of an eigenvalue problem, in Ref. 8 they were learnt by the RBM in an unsupervised way using a Monte Carlo sampling and the variational principle. While this approach was achieving chemical accuracy for small basis sets, the Monte Carlo sampling was repeatedly drawing the most dominant states (i.e. the Hartree-Fock determinant) and this was at the origin of a significant slow down of convergence for basis sets beyond the minimal

STO-3G. It was recently shown that this issue can be alleviated by using autoregressive neural networks, that allowed calculations with up to 30 spin orbitals.[11] Our numerical results presented below show that a simple RBM architecture used as a generative model can easily double this number. More in general it should be noticed that the representation of the wavefunction in the configuration space is strongly non-smooth (determinants with similar occupations can provide significantly different contributions to the wavefunction) and this could be challenging for ML regression approaches. To overcome this issue alternative methods use instead the high expressive power of deep neural networks to represent electronic structure wavefunctions in real-space;[12–15] as an advantage some of these techniques can achieve the complete basis set limit in a rather straightforward way but on the other side they require deep architectures involving the optimization of a large number of parameters and special care to keep into account the antisymmetry of the electronic wavefunction.

The antisymmetry is instead naturally included in the CI space which, however, grows unfavorably with the system size. This has lead to the development of a series of methods that select the excited determinants that contribute the most to the wavefunction, either based on perturbation theory[16] or Monte Carlo sampling.[16] More recently machine learning techniques have been coupled to these methods.[17–19] In this context Coe was the first to propose a Monte Carlo approach that explores the configuration space but, instead of explicitly computing the coefficient of each configuration, this is predicted by a regression neural network.[17] While Carleo and coworkers apply a neural network approach to "exactly" fit the wavefunction in the configuration space using the variational principle,[8] the alternative approaches of Refs. 17–19 are more qualitative and use supervised learning techniques.

In this work we propose an alternative approach named CIgen that uses generative machine learning to directly generate the configurations that contribute the most to the electronic wavefunction. This is done with the general aim of avoiding the exploration of the overwhelmingly large configuration space to search for the most important determinants. Notable examples of generative machine learning algorithms include the restricted Boltz-
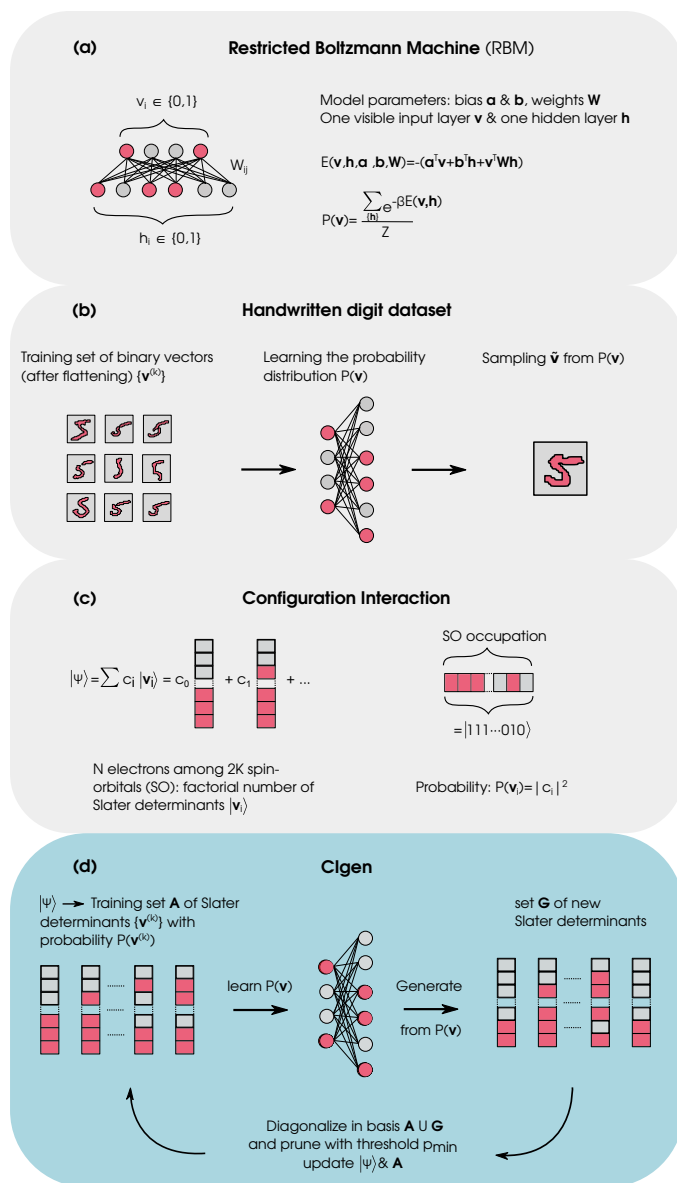
Figure 1: (a) Restricted Boltzmann machine (RBM) architecture consisting of one visible input layer and one hidden layer of binary values; for a given configuration $(\boldsymbol{v}, \boldsymbol{h})$ the parameters $(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{W})$ are used to define an energy function E and an associated Boltzmann-like probability density P. (b) As an example, the RBM can be trained on a set of handwritten digits and afterward used to generate new realistic ones; to this purpose the digit's images are flattened to become unidimensional binary vectors $\mathbf{v}^{(k)}$ where 1 and 0 correspond to the digit and background pixels, respectively. (c) The configuration interaction (CI) approach expands the wavefunction of a molecule as a a linear combination of excited Slater determinants, which can be represented as a sort of unidimensional binary image. (d) The CIgen algorithm presented in this work iteratively trains an RBM on the distribution of determinants in the current approximation of the wavefunction and subsequently uses it to expand it by generating new important contributions.

mann machines,[20,21] the variational autoencoders,[22] and the generative adversarial networks (GANs).[23] CIgen is based on RBMs, a type of generative neural network whose architecture is shown in Fig. 1(a). As for other generative models the RBM can learn in an unsupervised way the statistical distribution behind a series of input objects and then be used to generate new ones. A qualitative example is shown in Fig. 1(b): An RBM can be trained with a series of pictures, e.g. of handwritten digits, in practice represented as a flattened matrix of pixels and afterward used to generate realistic new realistic images of the same digit.

For a given molecule or material the excited Slater determinants are associated to an underlying probability distribution that could only be exactly evaluated by solving the Schrödinger equation to obtain the wavefunction. By representing the space of excited determinants simply as binary vectors (a sort of onedimensional binary image), the RBM is here iteratively trained using data from the current approximation of the wavefunction and subsequently used to generate new important determinants to improve the wavefunction approximation (see Fig. 1(c-d)).

Within the previous approach of Carleo and coworkers[5,8] the RBM was not properly used as a generative model but rather as a regression model for the wavefunction (to this purpose the RBM architecture was generalized to include complex weights); here we use instead the RBM as a model to qualitatively represent the probability distribution associated with the wavefunction, which is afterward used to generate the most likely configurations. In this respect the CIgen approach has some similarities with the use of RBMs to learn the statistical distribution of data from experimental measurements of quantum states and to subsequently generate new configurations for quantum averages.[21] Differently from selective CI or Monte Carlo CI our approach does not "explore" the huge determinant space to find significant contributions but rather directly generate them with the current approximation of the probability distribution associated with the RBM. Comparison with previous approaches will be further discussed below.

Results and discussion

Configuration interaction approach

Considering the non-relativistic N electron problem in the Born-Oppenheimer approximation, the configuration interaction method solves the Schrödinger equation for a fixed basis set by expanding the wavefunction in the following way:[10]

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{ra} c_a^r|\Phi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots \tag{1}$$

where $|\Phi_0\rangle$ is the Hatree-Fock ground state, $|\Phi_a^r\rangle$ is a singly excited Slater determinant from occupied spin orbital a to unoccupied spin orbital r, and all the other terms correspond to multiple excitations; while $|\Psi\rangle$ could denote any excited state of a given system here the discussion will be focused on the ground-state. When all the possible excited determinants are included in Eq. 1 the approach is called full configuration interaction (FCI) and the solution of the Schrödinger equation becomes exact for a given basis set. Within the "brute-force" FCI approach the coefficients of the expansion $c_0, c_a^r, \cdots$ are determined by computing the expectation value of the Hamiltonian $\langle\Psi|\hat{H}|\Psi\rangle$ and applying the variational principle. Since the total number of determinants grows as $\binom{2K}{N}$, where $2K$ is the number of spin-orbitals, the FCI approach becomes quickly unpractical for most applications. It is however well known that often the wavefunction can be accurately represented by a limited number of excited determinants and here a ML model is proposed to directly generate the important contributions.

Generative model

In this work, it is shown that restricted Boltzmann machine (RBM) can be used to efficiently generate the excited determinants that contribute the most to the wavefunction in Eq. 1.

An RBM, pictorically represented in Fig. 1, is a generative neural network consisting of one input layer of D visible binary units $\{v_i\} \in \{0,1\}^D$, one layer of P binary hidden units $\{h_j\} \in \{0,1\}^P$, and $D \times P$ weights $\{W_{ij}\}$ between both layers. Two bias vectors $\{a_i\}$ and $\{b_j\}$ are added to the visible and hidden layer, respectively.

By introducing an energy function of $\Lambda = \{\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{W}\}$ for a given configuration $\{\boldsymbol{v}, \boldsymbol{h}\}$ as

$$E(\boldsymbol{v}, \boldsymbol{h}, \Lambda) = -(\boldsymbol{a}^T \boldsymbol{v} + \boldsymbol{b}^T \boldsymbol{h} + \boldsymbol{v}^T \boldsymbol{W} \boldsymbol{h}), \tag{2}$$

and an inverse temperature $\beta = 1/T$, one can define the probability distribution associated with the RBM over the input configurations $\boldsymbol{v}$ to be

$$P(\boldsymbol{v}) = \frac{\sum_{\{\boldsymbol{h}\}} e^{-\beta E(\boldsymbol{v}, \boldsymbol{h})}}{\sum_{\{\boldsymbol{h}, \boldsymbol{v}\}} e^{-\beta E(\boldsymbol{v}, \boldsymbol{h})}}. \tag{3}$$

After training on a set of vectors $\boldsymbol{v}$ distributed according to $P(\boldsymbol{v})$, the RBM can be used to generate new vectors $\boldsymbol{v}$ according to this probability distribution. To this purpose the Gibbs sampling can be used:[24] Starting from an initial random trial vector as input, one can obtain a hidden-layer vector $\boldsymbol{h}$ using the conditional probability $p(h_i|v_i)$ and then obtain a new input-layer vector $\boldsymbol{v}$ using the conditional probability $p(v_i|h_i)$; the repetition of this operation a certain number of times forms a Markov chain that generates a vector $\boldsymbol{v}$ according to the probability $P(\boldsymbol{v})$.

For the purpose of this work the input vectors $\boldsymbol{v}$ represent the Slater determinants and their associated probability $P(\boldsymbol{v})$ should ideally be proportional to their contribution to the wavefunction (the square of the c coefficients in Eq. 1). The determinants are represented as binary vectors, where 1 denotes occupied and 0 unoccupied states, with size equal to the number of spin-orbitals (see Fig. 1). The architecture of the RBM used in this work is rather simple, with 2K (the number of spin orbitals) neurons in the visible and in the hidden layers. Given a certain fixed subspace of determinants, the Hamiltonian is diagonalized to obtain the wavefunction coefficients; the model is then trained with random configurations generated

according to the corresponding probability distribution by updating the RBM parameters with the contrastive divergence algorithm.[25] The training and generative procedure of an RBM are discussed in detail in Supplementary Material. The generation of new determinants and the retraining of the model are performed iteratively. Specifically, the CIgen algorithm performs the following steps:

1. Start: The configuration interaction singles and doubles (CISD) is used to generate an initial guess wavefunction.

2. Pruning: The determinants whose squared wavefunction coefficients (Eq. 1) are below a certain threshold p_{min} are pruned.

3. Training: The RBM model is trained only on the non pruned determinants but the Hartree-Fock determinant, which is typically associated to a very high probability, is not included in the training set (otherwise the ML would mainly generate the Hartree-Fock state in the following step).

4. Generation: The trained RBM is used to generate a set of new determinants, whose number is proportional to the number of determinants already included in the current approximation of the wavefunction. During this procedure determinants are automatically discarded if they are already included in the wavefunction, if they do not couple through single or double substitutions with the current determinant set, and if they do not have correct spin and point group symmetries.

5. Diagonalization: The Hamiltonian is diagonalized in the subspace that includes the newly generated determinants and new coefficients are obtained for Eq. 1.

6. Iterate: The procedure is repeated from step 2 until convergence of the energy is achieved.

Differently from previous approaches based on RBMs for quantum states,[5,8] CIgen does not require an RBM architecture generalized to include complex weights and, while the model

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still learns in an unsupervised way, the procedure is not based on the variational principle. While the training of a ML model based on the variational principle is more elegant and physically motivated,[5,8] the CIgen approach is less prone to overfitting as it does not aim to exactly fit the wavefunction.

Direct generation of single and double excitations

The CIgen algorithm is based on a rather straightforward way of using a generative neural network model to enlarge the configuration subspace of interest. However, the generative step (step 4 of the CIgen algorithm) often samples determinants that clearly cannot contribute to the wavefunction and this makes the overall procedure less efficient. For example, it is well known that a fixed set of determinants can only be coupled through the Hamiltonian to new determinants that differ by single and double substitutions. This observation, which has some subtle implications, is exploited by the Monte Carlo Configuration Interaction (MCCI) algorithm proposed by Greer *et al.*[26] In the MCCI algorithm, new determinants are sampled by randomly proposing single and double excitations of the determinants already included in the wavefunction set. At first sight this could seem a rather inefficient random procedure but in practice the important (highly contributing) determinants have often multiple connections to other important determinants through single and double substitutions and are much more likely to be sampled. To take advantage of this feature of the configuration space we developed a variant of our approach named CIgen-SD. Within this procedure a determinant Φ_1 is first randomly selected among those included in the current approximation of the wavefunction. Through the RBM a new determinant Φ_2 is then sampled and used exclusively to construct a transition probability matrix. Finally, a new determinant is proposed by exciting Φ_1 according to this probability matrix and the whole procedure is repeated several times. The CIgen-SD procedure is explained in details in Supplementary Material. The CIgen, CIgen-SD, and MCCI will be compared in the Numerical Results subsection.

Numerical Results

We now discuss the efficiency and accuracy of the CIgen approach by considering applications to molecular systems. To this purpose total energy calculations for the C_2, N_2, and H_2O molecules are performed for the 6-31G and cc-pVDZ basis sets considering the active spaces indicated in the third column of Table 1. For the largest system the number of spin orbitals is about double than what previously achieved with neural network quantum states.[11]

As a preliminary step it is important to discuss the effect of the temperature on the generative power of the RBM (see Eq. 3). Fig. S1 shows the convergence of the total energy of H_2O in the cc-pVDZ for three values of the temperature. The convergence of the CIgen approach is optimal at T=1 (chemical accuracy is achieved within 11 iterations) but sizeably slows down when T is increased to 5. In the limit of a very large temperature (T=500) the method performs poorly. Indeed, as explained in SM, the $T \to \infty$ limit leads to a completely random generation of determinants. This shows that for reasonable choices of the temperature the CIgen method actually learns the probability associated with the wavefunction and significantly speeds up the generation of the excited determinants with respect to random sampling.

We now consider the convergence of the total energy in the cc-pVDZ basis for the three molecules C_2, N_2, and H_2O in the cc-pVDZ basis and compare the perfomance of the CIgen and CIgen-SD algorithms with the MCCI algorithm. In all three cases the two CIgen variants considered here outperform the MCCI method. This is particularly true for the CIgen-SD approach that achieves chemical accuracy with a significantly smaller number of iterations.

The detailed results for the total energies of the molecules considered here are presented in Table 1, where CIgen-SD values are compared to coupled-cluster with singles, doubles and perturbative triples CCSD(T) and to FCI reference values. By considering a limited number of iterations (from a minimum of 9 for C_2 in 6-31G to a maximum of 17 for water in cc-pVDZ), CIgen-SD converges to FCI values within chemical accuracy. This is achieved by
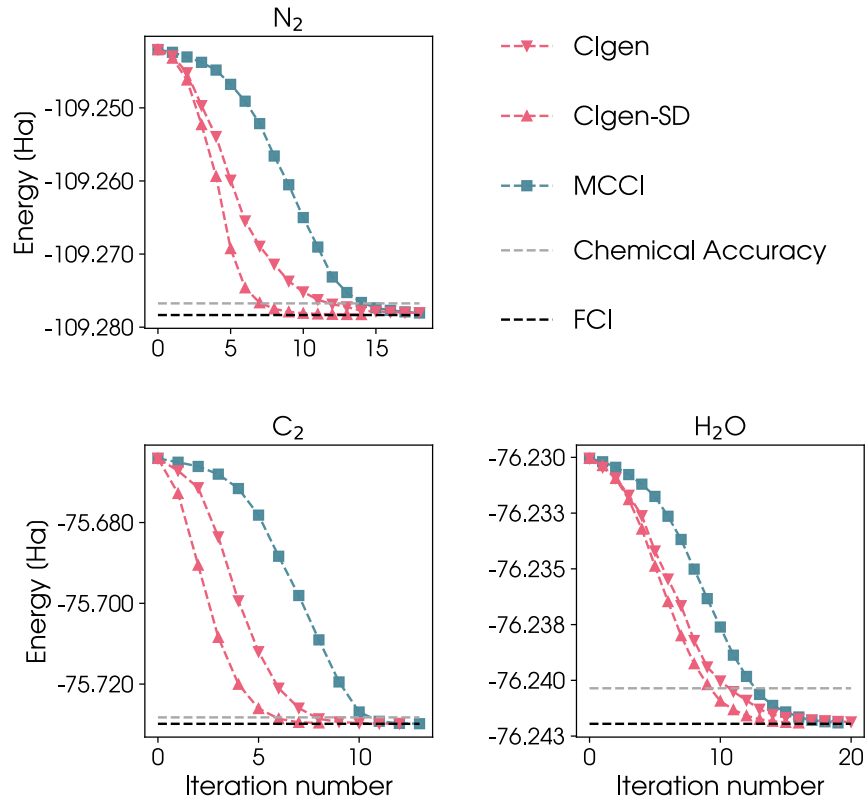
Figure 2: Total energy convergence for N_2, C_2, and H_2O in the cc-pVDZ basis set as a function of the number of iterations in the CIgen, CIgen-SD and MCCI algorithms. The full configuration interaction (FCI) reference values and the chemical accuracy threshold are represented by horizontal lines.

generating an excited determinant subspace that is significantly smaller than the full space. For example, for the molecule N_2 in the cc-pVDZ basis set only 3.5 million determinants are generated and included in the wavefunction out of the about 540 millions that would be allowed by spin and space symmetries. This significant reduction of two orders of magnitude in the number of determinants is not achieved by a search in the configuration space but rather by an iterative generation (and model training) of the determinants that contribute the most to the total energy.

As a final result in Fig. 3 we present a full binding curve for the N_2 molecule. This represent a much more challenging example since for large interatomic distances the binding is characterized by strong static correlation whose description could become problematic for several traditional quantum chemical approaches. This is the case of CCSD(T) that starting

Table 1: Total energies (Ha) for the different systems/basis sets considered here as obtained with the CIgen-SD method; reference FCI and CCSD(T) energies are provided for comparison purposes. The (N,K) column indicate the size of the active space, where N is the number of correlated electrons and K is the number of active molecular orbitals, and the N_{conv} column indicates the number of iterations to achieve convergence (i.e when the energy in two successive iterations differs by less than 10^{-5} Hartree).

System	Basis	(N,K)	$E_{CIgen-SD}$	$E_{CCSD(T)}$	E_{FCI}	N_{conv}
C_2	6-31G	(12,18)	-75.64416	-75.64415	-75.64418	12
N_2	6-31G	(14,18)	-109.10824	-109.10635	-109.10842	12
H_2O	6-31G	(10,13)	-76.12220	-76.12182	-76.12237	10
C_2	cc-pVDZ	(8,26)	-75.72982	-75.72781	-75.72984	9
N_2	cc-pVDZ	(12,27)	-109.27827	-109.27829	-109.27834	13
H_2O	cc-pVDZ	(8,23)	-76.24192	-76.24131	-76.24195	17

at around 1.8 Å produces a binding curve with an unphysical behavior. The CIgen approach well describes the N_2 binding curve at every distance and produces a curve in excellent agreement with FCI. The comparison with the CISD curve, which provides the starting training data for the generative model, shows clearly that CIgen recovers an increasing amount of electronic correlation energy as a function of the interatomic distance.
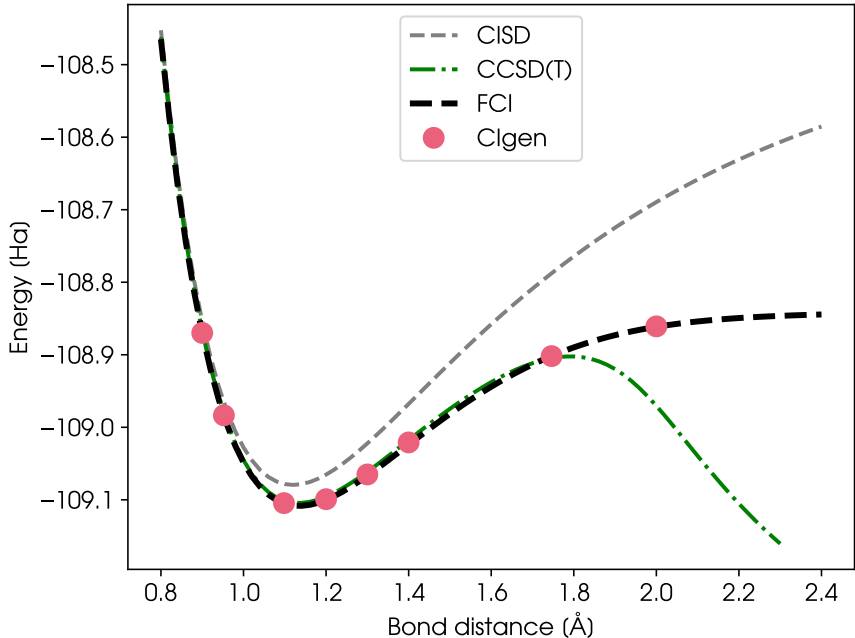

Figure 3: CIgen dissociation curve of N_2 in the 6-31G basis set compared to the CCSD(T), FCI, and CISD curves.

In summary we have shown how a generative model can be used to solve the Schrödinger equation by sampling the excited Slater determinants that contribute the most to the wavefunction. Numerical applications show that this approach is already competitive with previous approaches based on Monte Carlo sampling of the excited determinants[26] or on machine learning ansatzes to represent the wavefunction in the configuration space.[8,11] An improvement that should be addressed in future work involves the development of a generative model that intrinsically takes into account the symmetry of the determinants and, more in general, the properties of the determinants contributing to the wavefunction. It has already been shown that a sizeable improvement in the convergence speed can be achieved by directly generating the determinants that couple with double and single substitutions to the determinants already included in the wavefunction. In the current implementation, however, spin and spatial symmetries of the generated determinants are verified and enforced only *a posteriori*. The development of a generative machine learning model whose architecture keeps into account these symmetries would certainly increase the numerical efficiency of CIgen to possibly perform calculations with significantly larger numbers of spin orbitals.

Methods

Computational details

The equilibrium geometries of the molecules considered in this work are optimized at the CCSD(T) level of theory in the corresponding basis set (6-31G or cc-pVDZ) and can be obtained from the Computational Chemistry Comparison and Benchmark DataBase.[27] The reference results for these molecules at the CCSD(T) and FCI level of theory (Table 1 and Figs. 2-3) have been obtained from the Molpro code.[28,29]

The electronic structure part of our implementation (specifically the diagonalization of the Hamiltonian in the space of the generated determinants) is based on the Quantum Package code.[30] The selection of the determinants to be included in the wavefunction in Eq.

1 is based on an acceptance threshold of 10^{-12} on the squared coefficients.

Acknowledgement

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