Approaching the Full Configuration Interaction Ground State from an Arbitrary Wavefunction with Gradient Descent and Quasi-Newton Algorithms

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(Dated: October 6, 2020)

We discuss gradient descent and quasi-Newton algorithms to optimize the full configuration interaction (FCI) ground state wavefunction starting from an arbitrary reference state $|0\rangle$. In particular, we show that the energies obtained along the optimization path can be evaluated in terms of expectation values of $|0\rangle$, thus avoiding explicit storage of intermediate wavefunctions. We show an application of the algorithm with reference wavefunctions constructed as linear combinations of non-orthogonal determinants.

I. INTRODUCTION

In principle, all the chemical properties of molecular systems can be determined from knowledge of the eigenstates of the Hamiltonian operator. The full-configuration interaction (FCI) wavefunction constitutes a prominent paradigm of quantum chemistry [1]: it provides the exact solution of the Schrödinger equation on a basis of suitably selected $N$-electron wavefunctions. While finding the FCI ground state wavefunction is algorithmically easy, the number of degrees of freedom in it increases exponentially with system size. Therefore, one of the central goals of the quantum chemistry community is to develop approximations that can yield properties of similar quality as that from the FCI ground state while reducing significantly the computational cost entailed.

In this work we shall consider the optimization of the FCI ground state wavefunction in an implicit way, as described below. Given a matrix representation of the Hamiltonian operator $H$ and a vector representation of a starting reference wavefunction $|0\rangle$, potent algorithms (with that from Davidson [2] being a prominent example) have been developed to optimize the FCI ground state wavefunction $|\Psi_{\text{FCI}}\rangle$ while minimizing the number of matrix-vector operations and the number of intermediate wavefunctions. Nevertheless, the dimension of the FCI problem renders this approach possible only for relatively small systems.

In order to reach the FCI ground state, we parametrize the FCI ground state wavefunction in terms of the reference $|0\rangle$ and its orthogonal complement, yet an explicit representation of the latter is not necessary, as shown below. Instead of working with an explicit vector representation of the parametrized wavefunction in the full Hilbert space of the system, we work out explicit expressions, in closed form, of the energy along optimization paths defined by gradient descent and quasi-Newton algorithms. We show that such approximations to the FCI energy can in fact be written as functionals of the reference wavefunction itself.

Avoiding the explicit vector representation allows us to consider systems for which the dimension of the Hilbert space is larger than the disk or memory available in current computational facilities. There is another important reason to avoid the explicit vector representation, which actually constitutes the motivation for this manuscript. We shall consider classes of wavefunctions for which a vector representation in some convenient orthonormal $N$-electron basis is not available, and the computational cost of evaluating it would be proportional to the dimension of the Hilbert space. A specific example that we shall consider are reference states written as linear combination of a few determinants that are, in general, non-orthogonal:

$$|0\rangle = \sum_q f_q |\Phi_q\rangle.$$  

In that case the orthogonal complement cannot be constructed implicitly and the vector representation in a basis of, e.g., orthonormal Slater determinants can be constructed only at great expense. This class of wavefunctions occur in non-orthogonal configuration interaction (NOCI) [3] as well as in symmetry-projected Hartree–Fock methods [4].

The rest of this manuscript is organized as follows. In Sec. II we describe how we parametrize the FCI ground state wavefunction and describe the gradient descent and quasi-Newton optimization algorithms considered. In Sec. III we discuss the application of the method in an $H_4$ ring and in the dissociation profile of the $N_2$ molecule. Finally, in Sec. IV we provide some closing remarks.

II. THEORY

We parametrize the FCI ground state $|\Psi_{\text{FCI}}\rangle$ using an exponential, non-Hermitian ansatz of the form

$$|\Psi\rangle = \exp(\hat{Z})|0\rangle,$$  

$$\hat{Z} = \sum_x Z_x |x\rangle\langle 0|,$$  

where $|0\rangle$ is the reference wavefunction and $|x\rangle$ labels an orthonormal state in the orthogonal complement of $|0\rangle$. 

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The FCI ground state can be reached after an unconstrained optimization in the parameters \(Z\). An important ingredient of this work is that an explicit construction of the states \(\{|x\}\) will not be necessary. We assume in what follows that \(\langle 0| \Psi_{\text{FCI}}| 0 \rangle \neq 0\).

Given \(Z\), the energy of \(|\Psi\rangle\) can be evaluated as

\[
E[Z] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle 0 | \exp(\hat{Z}^T) H \exp(\hat{Z}) | 0 \rangle \quad (0 | \exp(\hat{Z}^T) \exp(\hat{Z}) | 0 \rangle = \frac{H^0_0 + H^0_0 Z_x + Z^x H^y_y Z_y + Z^2 H^y_y Z_y}{1 + Z^2 Z_x},
\]

where Einstein summation is implied and the indices \(x, y\) run only over the orthogonal complement of \(0\). Here, we have used the fact that \(\hat{Z}^2 |0\rangle = 0\). We have also assumed a real wavefunction \(|0\rangle\) and real coefficients \(Z\), as we do throughout this work.

The energy gradient with respect to \(Z\), evaluated at \(Z = Y\) is given by

\[
g_z = \frac{\partial E[Z]}{\partial Z_z} \bigg|_{z = y} = \frac{2H^0_0 + 2H^0_0 Y_y - 2E[Y]Y_y}{1 + Y^0 Y_y}.
\]

Along the optimization paths described in the next subsections a line search is needed to minimize the energy of \(E[Z + sY]\), with \(Z\) being the current position and \(Y\) the search direction, with respect to the step size \(s\). Explicitly, \(E[Z + sY]\) becomes

\[
E[Z + sY] = \frac{E[Z](1 + Z^x Z_x) + s(H^x_x + Z^y H^y_y)Y_x + sY^x(H^0_x + H^y_y Z_y) + s^2 Y^x H^y_y Y_y}{(1 + Z^2 Z_x) + sZ^x Y_x + sY^x Z_x + s^2 Y^x Y_x}.
\]

This is a rational equation in \(s\) of the form

\[
c + bs + as^2 \quad f + es + ds^2.
\]

Let \(s_*\) be the value of \(s\) that extremizes \(E[Z + sY]\). It is straightforward to show that \(s_*\) takes the form

\[
s_* = \frac{(cd - af) \pm \sqrt{(cd - af)^2 - (ae - bd)(bf - ce)}}{(ae - bd)}.
\]

For convenience, we shall introduce the quantities \(f_1 = H^0_0, f_2 = H^0_0 H^0_0, f_3 = H^0_0 H^y_y H^0_0, \) etc. Note that all those matrix elements can be evaluated in terms of expectation values from the reference wavefunction \(|0\rangle\). For instance,

\[
f_2 = \langle 0 | H^2 | 0 \rangle - \langle f_1 \rangle | 0 | H | 0 \rangle,
\]

\[
f_3 = \langle 0 | H^3 | 0 \rangle - \langle f_1 \rangle | 0 | H^2 | 0 \rangle - \langle f_2 \rangle | 0 | H | 0 \rangle.
\]

**A. Gradient Descent**

We begin at \(Z_0 = 0\) with \(|\Psi_0\rangle = |0\rangle\). The gradient at \(Z_0\) is

\[
(g_0)_x = \alpha_0 H^0_x,
\]

with \(\alpha_0 = 2\).

In a standard gradient descent implementation a line search would be performed along \(-g_0\). It is common practice to accept a step size that satisfies Wolfe conditions to avoid the potentially expensive full line search. In our case, we aim to perform a full line search, as we may only be able to afford a few steps. The optimal step size \(\sigma_*\) can be easily found given the rational form of \(E[Z]\) discussed above. Therefore, \(Z_1 = -\sigma_* g_0\) and \(|\Psi_1\rangle\) becomes

\[
|\Psi_1\rangle = e^{-\sigma_* g_0} |0\rangle.
\]

An explicit expression for \(E_1\) is given by

\[
E_1 = \frac{\langle \Psi_1 | H | \Psi_1 \rangle}{\langle \Psi_1 | \Psi_1 \rangle} = \frac{f_1 - 4\sigma_* f_2 + 4\sigma_*^2 f_3}{1 + 4\sigma_*^2 f_2},
\]

with

\[
\sigma_* = \frac{(4f_3 - 4f_1 f_2) \pm \sqrt{(6f_2^2 + (4f_3 - 4f_1 f_2)^2)}}{-16f_2^2}.
\]

Note that \(E_1\) is a functional of \(|0\rangle\) which can be determined after evaluation of \(f_1, f_2,\) and \(f_3\). (This is an interesting functional in itself. One may consider optimizing \(E_1\) with respect to the reference wavefunction parameters \(|0\rangle\), though we have not attempted that in this work.)

We now proceed to take another step. The gradient at \(Z_1 = -\sigma_* g_0\) is given by

\[
(g_1)_x = \alpha_1 H^0_x + \beta_1 H^y_y H^0_y
\]

with

\[
\alpha_1 = \frac{2 + 4\sigma_* E_1}{1 + 4\sigma_*^2 f_2},
\]

\[
\beta_1 = \frac{-4\sigma_*}{1 + 4\sigma_*^2 f_2}.
\]

After looking for the optimal step size \(\tau_*\) (i.e., minimizing \(E[-\sigma_* g_0 - \tau_* g_1]\) with respect to \(\tau\), \(|\Psi_2\rangle\) becomes

\[
|\Psi_2\rangle = e^{-\sigma_* g_0 - \tau_* g_1} |0\rangle.
\]

An explicit expression for \(E_2\) is given below
\[ E_2 = \frac{\langle \Psi_2 | H | \Psi_2 \rangle}{\langle \Psi_2 | \Psi_2 \rangle} = \frac{E_1 (1 + 4\alpha_2^2 f_2) - 2\tau_x (\alpha_1 f_2 + \beta_1 f_3) + 4\sigma_\tau (\alpha_1 f_3 + \beta_1 f_1) + \tau_x^2 (\alpha_1^2 f_3 + 2\alpha_1 \beta_1 f_4 + \beta_1^2 f_5)}{(1 + 4\alpha_2^2 f_2) + 4\sigma_\tau (\alpha_1 f_2 + \beta_1 f_3) + \tau_x^2 (\alpha_1^2 f_2 + 2\alpha_1 \beta_1 f_3 + \beta_1^2 f_4)}. \]  

(16)

A closed-form expression for \( \tau_x \) can be deduced from the rational form of \( E_2 \) as a function of \( \tau_x \), as described before. \( E_2 \) is also a functional of \( |0\rangle \) that can be assembled after evaluation of \( f_1, \ldots, f_5 \).

A third step would require the evaluation of \( g_2 \). It is straightforward to see that \( g_2 \) takes the form

\[ (g_2)_x = \alpha_2^2 H_x^0 + \beta_2 H_y^0 + \gamma_2 H_y^0 H_z^0. \]

(17)

Therefore, \( E_3 \) would be also a functional of \( |0\rangle \) that can be determined after evaluation of \( f_1, \ldots, f_7 \). Subsequent steps require the evaluation of higher order \( f_k \) values.

At this point we note that the gradient descent approach described above can, in principle, be used to converge to the true eigenfunction of the Hamiltonian \( H \) as opposed to its representation in some finite \( N \)-electron basis \( H \). It would involve replacing the expectation values \( \langle 0 | H^k | 0 \rangle \) with \( \langle 0 | H^k | 0 \rangle \), with everything else holding. This, however, requires further work given that individual integrals appearing in \( H^2 \) (and higher powers) diverge when evaluated with Gaussian basis functions.

As a second remark, we note that the evaluation of other expectation values can be done in the same way as the energy. For instance, the expectation value of \( X \), after the first gradient descent step, is given by

\[ X_1 = \frac{\langle \Psi_1 | X | \Psi_1 \rangle}{\langle \Psi_1 | \Psi_1 \rangle} = \frac{f_1^2 - 4\sigma_x f_2 \rho + 4\sigma_x^2 f_2^2}{1 + 4\sigma_x^2 f_2^2}, \]

(18)

with \( f_1^2 = X_0, f_2^2 = \frac{1}{2} (X_0^2 - H_0 X_0^2), f_3^2 = H_0 X_0^2 H_0^0 \). This is also a functional of \( |0\rangle \) since

\[ f_2^2 = \frac{1}{2} \langle 0 | X H + H X | 0 \rangle - f_1 \langle 0 | X | 0 \rangle, \]

(19)

\[ f_3^2 = \frac{1}{2} \langle 0 | H X H | 0 \rangle - \frac{1}{2} f_1 \langle 0 | H X + X H | 0 \rangle - f_2 \langle 0 | H | 0 \rangle. \]

(20)

### B. Quasi-Newton

Because the convergence of the gradient descent algorithm is slow, we now consider a quasi-Newton optimization. In a quasi-Newton approach \cite{11}, it is customary to start from an initial inverse Hessian \( B_0 \), which need only be an approximation to the true Hessian. At each step along the optimization, the search direction \( p_k \) is determined from \( B_k p_k = -g_k \), rather than setting \( p_k = -g_k \) as in the gradient descent approach. In this work we choose to set \( B_0 = I \) to keep things as simple as possible: under such conditions, a quasi-Newton algorithm can still be fully defined in terms of \( |0\rangle \). Naturally, if a better \( B_0 \) is used the number of iterations required to reach convergence is expected to decrease.

Just as in the gradient descent approach, after defining a search direction \( p_k \), a line search is performed along it. Commonly, a step size that satisfies Wolfe conditions is accepted. We choose, however, to carry a full line search as in the gradient descent algorithm.

Because \( B_0 = I \), it follows that the first step coincides with that from the gradient descent approach, and \( E_1 \) remains unchanged. The gradient \( g_1 \) is also the same as in gradient descent (see Eq. 12). The direction \( p_1 \) is determined from \( p_1 = -B_1 g_1 \), with \( B_1 \) constructed using a quasi-Newton update formula.

We shall use the Broyden-Fletcher-Goldfarb-Shanno (BFGS) \cite{11} update as an example. Let

\[ s_0 = Z_1 - Z_0 = Z_1, \]

(21)

\[ y_0 = g_1 - g_0, \]

(22)

which would yield \( s_0 = -\sigma_x g_0 \) and \( (y_0)_x = (\alpha_1 - \alpha_0) H_x^0 + \beta_1 H_y^0 H_z^0 \). With \( \rho_0 = 1/|s_0|^2 \langle y_0 | y_0 \rangle \), the BFGS update takes the form

\[ (B_1)_x = \frac{(B_0)_x - \rho_0 (B_0)^y (y_0)_x (s_0)_x - \rho_0 (s_0)_y (y_0)^x (B_0)_x^y + \rho_0^2 (s_0)^2 y_0 (s_0)_x (y_0)_x)}{\rho_0 + (y_0)_x^2 (B_0)_x^y (y_0)_y} \]

(23)

We now carry an explicit evaluation of \( p_1 = -B_1 g_1 \). We note that

\[ \rho_0^{-1} = -2\sigma_x (\alpha_1 - \alpha_0) f_2 - 2\sigma_x \beta_1 f_3, \]

\[ \langle y_0 | y_0 \rangle = (\alpha_1 - \alpha_0)^2 f_2 + 2(\alpha_1 - \alpha_0) \beta_1 f_3 + \beta_1^2 f_4, \]

\[ \langle s_0 g_1 \rangle = (\alpha_1 - \alpha_0)^2 g_2 + 2(\alpha_1 - \alpha_0) \beta_1 g_3 + \beta_1^2 g_4, \]

\[ \langle y_0 g_1 \rangle = (\alpha_1 - \alpha_0)^2 g_2 + 2(\alpha_1 - \alpha_0) \beta_1 g_3 + \beta_1^2 g_4, \]

(24)

Therefore, \( p_1 \) takes the form

\[ (p_1)_x = \alpha_1^2 H_x + \beta_1^2 H_x^0 H_y^0, \]

(24)

with

\[ \alpha_1' = \alpha_1 - 2\sigma_x \beta_1 \rho_0 (s_0)_y + \rho_0 \langle s_0 | g_1 \rangle, \]

(25)

\[ \beta_1' = \beta_1 - \rho_0 \langle s_0 | g_1 \rangle. \]

(26)

Given that \( p_1 \) takes the same functional form as \( g_1 \), we conclude that \( E_2 \) determined from the BFGS approach is also a functional of \( f_1, \ldots, f_5 \). Namely, \( E_2 \) would take the same form as Eq. 16 with \( \alpha_1 \rightarrow \alpha_1' \) and \( \beta_1 \rightarrow \beta_1' \). Further quasi-Newton steps can also be cast as functionals of \( |0\rangle \), in the same way as in the gradient descent algorithm.
III. RESULTS AND DISCUSSION

We proceed to discuss the application of the optimization algorithms described above in two systems: an H$_4$ ring and the N$_2$ molecule.

A. H$_4$ ring

We consider a system of 4 H atoms placed along a ring of radius $r = 3.3$ bohr [12], with the arrangement depicted in Fig. 1. For $\theta \approx 24$ deg, the system consists of two weakly interacting H$_2$ molecules near their equilibrium geometry. Conversely, for $\theta = 90$ deg the 4 H atoms form a square and the system has a strong multireference character. In scanning $\theta$ in the range between 20 deg and 90 deg the system evolves from a weak to a strong correlation regime. Our calculations in this system were performed by explicitly constructing the vector representation of the considered wavefunctions; this allows us to study the convergence behavior of the gradient descent and quasi-Newton algorithms.

![FIG. 1: The H$_4$ system described in Ref. 12 consists of four H atoms placed along a ring of radius $r = 3.3$ bohr, controlled by an angle $\theta$. At $\theta \approx 24$ deg the system corresponds to two weakly interacting H$_2$ units near their equilibrium geometry.](image)

The improvement upon the RHF energy obtained with the first gd step is quite significant: the error is reduced by nearly a third at $\theta = 90$ deg and by an order of magnitude in the equilibrium region. The second step (either gd or qn) also yields a very significant improvement on RHF, with the qn step leading to a substantial improvement over the gd step. In the case of UHF and SUHF, the improvement after the first and second steps is very modest near $\theta = 90$ deg, although the improvement near the equilibrium region is still substantial. Around $\theta \approx 50$ deg, the first step correction to RHF leads to a lower energy than the first step correction to UHF even when the reference wavefunction itself is lower in energy. As more steps are taken, the expectation is that the qn algorithm will outperform the gd algorithm as the former converges linearly while the latter should approach quadratic convergence [7].

We show in Fig. 2 the convergence profile of the gd and qn algorithms on top of the RHF, UHF, and SUHF wavefunctions at $\theta = 24$ deg (top) and $\theta = 90$ deg (bottom). At $\theta = 24$ deg, convergence is relatively fast: with gd, 10 steps are sufficient to converge the energy to $10^{-5}$ hartree, while 5 steps are enough with the qn algorithm. At $\theta = 90$ deg the profiles are very different. While convergence starting from the SUHF reference wavefunction is quite fast, a starting RHF or UHF wavefunction leads to much slower convergence. In particular, the gd algorithm from UHF converges extremely slowly. The qn algorithms do recover a faster convergence rate after 15 or so iterations.

B. Dissociation of N$_2$

We now consider the dissociation profile of N$_2$ with a cc-pVDZ basis set. Reference FCI (with a frozen-core approximation) results for this system are available from Ref. 13. In Fig. 3, we show the profiles obtained with RHF, UHF, and SUHF, as well as the corresponding profiles after a single gd step is performed. Complementary to the RHF and UHF results we show configuration interaction singles and doubles (CISD) results starting from RHF and UHF, calculated using Gaussian 16 [14]. It is straightforward to realize that the RHF+1 and UHF+1 energies should be above the corresponding RCISD and UCISD ones.

We emphasize that, in this case, we have produced the energies after a single gd step without a formal vector representation of the starting reference wavefunctions (in a basis of Slater determinants, the dimension of the FCI vector is $\approx 1.4 \times 10^{12}$). In evaluating the energy after the single gd step we computed $\langle 0|H^2|0 \rangle$ for a reference wavefunction that is either a single Slater determinant or a linear combination of non-orthogonal determinants. In both cases the evaluation can be completed with a computational effort of $O(N^3 M^3)$ (with $N$ being the number of electrons and $M$ the number of virtual orbitals). For this system we do not show results after a second step as
we do not currently have code that can evaluate up to \( \langle 0 | H | 0 \rangle \).

In the case of RHF, a single gd step recovers \( \approx 50\% \) of the correlation energy near equilibrium; the same is true with the SUHF wavefunction. As expected, RCISD and UCISD energies are significantly lower than RHF+1 and UHF+1, although the curves are quite parallel to each other.

### IV. CONCLUSIONS

We have presented gradient descent and quasi-Newton algorithms to reach the FCI ground state energy starting from an arbitrary reference wavefunction. In particular, we have avoided an explicit representation of the wavefunction during the optimization process, opting to write the energies, at each step in the optimization, as functionals of the reference wavefunction. The resulting functionals have some useful properties:
• They are independent of the form of the reference wavefunction. Therefore, they provide an unbiased way to compare how different wavefunctions evolve towards the FCI ground state along the optimization path.

• The functional forms are independent of the specific wavefunction parameters. That is to say, if the reference wavefunction is chosen as a single Slater determinant, then any Slater determinant (as long as it is not orthogonal to the FCI ground state) can be used with the functional forms provided.

Given that the evaluation of the matrix elements $\langle 0 | H^k | 0 \rangle$ can become quite expensive as $k$ increases, we realize that practical applications may be limited to the first few steps. In this case, a better starting initial inverse Hessian (as opposed to $B = I$) can lead to substantially improved results. We are currently investigating this possibility.

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments

This work was supported by a generous start-up package from Wesleyan University.

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