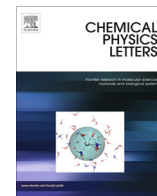




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Research paper

A general second order complete active space self-consistent-field solver for large-scale systems

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ABSTRACT

We present a new second order complete active space self-consistent field implementation to converge wavefunctions for both large active spaces and large atomic orbital (AO) bases. Our algorithm decouples the active space wavefunction solver from the orbital optimization in the microiterations, and thus may be easily combined with various modern active space solvers. We also introduce efficient approximate orbital gradient and Hessian updates, and step size determination. We demonstrate its capabilities by calculating the low-lying states of the Fe(II)-porphine complex with modest resources using a density matrix renormalization group solver in a CAS(22,27) active space and a 3000 AO basis.

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1. Introduction

Multiconfigurational electronic structure is widely found across chemistry [1]. The complete active space self-consistent field (CASSCF) is a standard tool to describe multiconfigurational electronic structure problems [1,2]. The CASSCF wavefunction further forms the starting point for more accurate treatments, including multireference perturbation theory and configuration interaction methods [3]. Because of its importance, much effort has been devoted to efficient CASSCF algorithms in the last decades [4–16].

A well-known numerical challenge in CASSCF is to converge the self-consistent wavefunction. For this reason, many early investigations focused on second order optimization techniques, which demonstrate superior convergence to pure gradient or super-CI formulations [4,5,7,8,6,9–11]. Unfortunately, these early implementations were optimized for modest AO basis sets, because they transformed the integrals to the current set of CASSCF orbitals in each iteration, incurring significant computational cost and $\mathcal{O}N^4$ disk storage. To extend CASSCF algorithms to large AO bases, several strategies have been explored [12–15]. For example, density-fitted CASSCF [12,13] and Cholesky decomposition CASSCF [14] both approximate the AO integrals to achieve significant savings in the integral transformation cost and disk storage. GPU-based AO-driven CASSCF implementations [15,17] further can handle very large numbers of AO functions, although these have not yet been extended to second order optimization. Although AO-driven

algorithms typically require more floating point operations than MO-driven approaches, they are favourable for modern computers, due to their low IO and communication costs. In this work, our first motivation is to present a new AO-driven algorithm that can handle large AO basis sets without integral approximations, and also provide second order convergence. Our algorithm may easily be combined with density-fitting or Cholesky decomposition, although this is not a focus of this paper.

A second motivation is associated with the need to extend traditional CASSCF implementations to larger active spaces. In traditional CASSCF, full configuration interaction (FCI) is used as the active space solver. However, due to the exponential scaling of FCI, it is limited to small complete active spaces (CAS), usually no more than CAS(16,16) (16 electrons in 16 orbitals). However, there are now several techniques which can be used to replace the FCI solver [18–23]. Two of the more commonly used ones are the density matrix renormalization group (DMRG) [18] and full configuration interaction quantum Monte Carlo (FCIQMC) [20,21]. These can handle correlated active spaces with many tens of orbitals, and in some cases even more [19]. While implementations of DMRG and FCIQMC in the CASSCF algorithm exist [24–31] they do not yet simultaneously provide second order convergence and the ability to treat very large numbers (i.e. 1000s) of AO's. The implementation we present can be straightforwardly interfaced to any external active space solver and thus fills this gap. In the current work, we will use FCI and DMRG as the active space solvers. (An earlier FCIQMC-CASSCF calculation, reported in Ref. 29, used the two-step version of our implementation that we describe here).

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In Section 2, we describe the formulation of our CASSCF algorithm, including the approximate orbital gradient and Hessian updates, and orbital optimization method. In Section 3 we carefully study the convergence properties and performance of our algorithm for several benchmark molecules, within our open-source program package PySCF [32]. Finally, as an example of a more challenging large scale problem, we use FCI and DMRG active space solvers and our CASSCF implementation to converge the Fe(II)-porphine singlet, triplet and quintet ground states. Our largest calculation uses a 22 electron, 27 orbital active space and almost 3000 AO basis functions.

2. Algorithm

2.1. Theory

In this section, we first summarize the relevant formulae for the optimization of the CASSCF wavefunction. Given the spin-free electronic Hamiltonian,

$$H = \sum_{ij} h_{ij} E_j^i + \frac{1}{2} \sum_{ijkl} (ij|kl) (E_j^i E_l^k - \delta_{jk} E_l^i) \quad (1)$$

$$E_j^i = a_{i\alpha}^\dagger a_{j\alpha} + a_{i\beta}^\dagger a_{j\beta} \quad (2)$$

the CASSCF energy can be written as a function of the CI coefficients \mathbf{c} and the unitary orbital transformation matrix \mathbf{U} ,

$$E = H_{ijkl} \Gamma_{ijkl} \quad (3)$$

$$H_{ijkl} = V_{ijkl} U_{pi} U_{qj} U_{rk} U_{sl} \quad (4)$$

$$V_{pqrs} = \frac{1}{2(N_e - 1)} h_{pq} \delta_{rs} + \frac{1}{2(N_e - 1)} h_{rs} \delta_{pq} + \frac{1}{2} (pq|rs) \quad (5)$$

$$\Gamma_{ijkl} = \langle I | (E_j^i E_l^k - \delta_{jk} E_l^i) | J \rangle c_i c_j \quad (6)$$

where the Einstein summation convention is implied. Defining a Lagrangian with normalization constraints for \mathbf{c} and \mathbf{U} ,

$$F(\mathbf{R}, \mathbf{c}) = E(\mathbf{R}, \Gamma) - \mathcal{E}(\mathbf{c}^\dagger \mathbf{c} - 1) \quad (7)$$

$$\mathbf{U} = \exp(\mathbf{R}) \quad (8)$$

$$\mathbf{R} = -\mathbf{R}^\dagger \quad (9)$$

minimizing the energy is a non-linear optimization problem for \mathbf{R} , \mathbf{c} , where the stationary conditions are

$$\frac{\partial F}{\partial c_i} = 0 \quad (10)$$

$$\frac{\partial F}{\partial R_{pq}} = 0 \quad (11)$$

Because the energy is quadratic in the CI coefficients, the CI coefficients, holding the orbitals fixed, can be obtained by solving the standard CI eigenvalue problem

$$\langle I | (H - \mathcal{E}) | J \rangle c_j = 0 \quad (12)$$

A Newton step for the orbitals, holding the CI coefficients fixed, corresponds to solving the equations

$$\mathcal{H}^{oo} \mathbf{R}^1 + \mathcal{G}^o = 0 \quad (13)$$

$$\mathcal{G}_{pq}^o = \frac{\partial F}{\partial R_{pq}} = \frac{\partial H_{ijkl}}{\partial R_{pq}} \Gamma_{ijkl} \quad (14)$$

$$\mathcal{H}_{pq,rs}^{oo} = \frac{\partial^2 F}{\partial R_{pq} \partial R_{rs}} = \frac{\partial^2 H_{ijkl}}{\partial R_{pq} \partial R_{rs}} \Gamma_{ijkl} \quad (15)$$

The simplest approach to CASSCF optimization is to alternately solve (12) and (13) for the CI coefficients and for the orbitals. This simple alternating scheme is known as the two-step optimization method. Unfortunately, even when the Newton steps are carried out exactly, for example, by using the exact orbital Hessian in Eq.

(13), the two-step method suffers from slow convergence due to the neglect of coupling between the CI and orbital optimization problems. It is thus not usually considered a true second order convergent algorithm.

The more sophisticated, one-step, optimization methods aim to approximate the joint CI displacement and orbital Newton steps, corresponding to solving

$$\begin{pmatrix} \mathcal{H}^{cc} & \mathcal{H}^{co} \\ \mathcal{H}^{oc} & \mathcal{H}^{oo} \end{pmatrix} \begin{pmatrix} \mathbf{c}^1 \\ \mathbf{R}^1 \end{pmatrix} + \begin{pmatrix} \mathcal{G}^c \\ \mathcal{G}^o \end{pmatrix} = 0 \quad (16)$$

where the Hessian matrices are

$$\mathcal{H}_{ij}^{cc} = \frac{\partial^2 F}{\partial c_i \partial c_j} = 2 \langle I | (H - \mathcal{E}) | J \rangle \quad (17)$$

$$\mathcal{H}_{i,pq}^{co} = \mathcal{H}_{pq,i}^{oc} = \frac{\partial^2 F}{\partial c_i \partial R_{pq}} = \frac{\partial H_{ijkl}}{\partial R_{pq}} \frac{\partial \Gamma_{ijkl}}{\partial c_i} \quad (18)$$

Here, the first row of the coupled Eq. (16)

$$\mathcal{H}^{cc} \mathbf{c}^1 + \mathcal{H}^{co} \mathbf{R}^1 + \mathcal{G}^c = 0 \quad (19)$$

can be rewritten as a CI response problem

$$\mathbf{H}^0 \mathbf{c}^1 + \mathbf{H}^R \mathbf{c}^0 = \mathbf{E}^0 \mathbf{c}^1 \quad (20)$$

since

$$(\mathcal{H}^{co} \mathbf{R}^1)_i = 2 H_{ijkl}^R \langle I | (E_j^i E_l^k - \delta_{jk} E_l^i) | J \rangle c_j^0 \quad (21)$$

$$\mathcal{G}_i^c = 2 \langle I | (\mathbf{H}^0 - \mathbf{E}^0) | J \rangle c_j^0 = 0 \quad (22)$$

where the first order Hamiltonian \mathbf{H}^R is obtained from the chain rule

$$H_{ijkl}^R = \frac{\partial H_{ijkl}}{\partial R_{pq}} R_{pq}^1 = V_{pjkl} R_{pi}^1 + V_{ipkl} R_{pj}^1 + V_{ijpl} R_{pk}^1 + V_{ijkp} R_{pl}^1 \quad (23)$$

The second row of Eq. (16)

$$\mathcal{H}^{oo} \mathbf{R}^1 + \mathcal{H}^{oc} \mathbf{c}^1 + \mathcal{G}^o = 0 \quad (24)$$

can be interpreted as the orbital Newton problem with dressed gradients

$$\mathcal{H}^{oo} \mathbf{R}^1 = -\tilde{\mathcal{G}}^o \quad (25)$$

$$\tilde{\mathcal{G}}_{pq}^o = \mathcal{G}_{pq}^o + \mathcal{H}^{oc} \mathbf{c}^1 = \mathcal{G}_{pq}^o + \frac{\partial H_{ijkl}}{\partial R_{pq}} \Gamma_{ijkl}^{-1} \quad (26)$$

$$\Gamma_{ijkl}^{-1} = \frac{\partial \Gamma_{ijkl}}{\partial c_i} c_i^1 \quad (27)$$

The CI coefficient and orbital optimization problems are thus coupled through the first order \mathbf{H}^R in Eq. (20) and the first order 2-particle density matrix Γ^1 in Eq. (25).

In principle, in the one-step method, the true CI displacement requires solving the response Eq. (20) exactly. This is how some early versions of one-step optimization in CASSCF were implemented. However, if an iterative procedure is used to determine the CI eigenstate in Eq. (12), then a single (or few) steps of the same iterative procedure, with the modified Hamiltonian $\mathbf{H}^0 + \mathbf{H}^R$ and initial eigenstate guess of \mathbf{c}^0 , can be used to determine an approximate \mathbf{c}^1 . For example, a single Davidson iteration [33] with these quantities yields

$$\mathbf{c}^1 \approx -[\text{diag}(\mathbf{H}^0 - \mathbf{E}^0)]^{-1} \mathbf{H}^R \mathbf{c}^0 \quad (28)$$

as an approximate solution of Eq. (20). The well-known MCSCF implementation by Werner and Knowles [8], uses this type of approximation. In our implementation, we also use a few iterations of the active space solver to determine an approximate update \mathbf{c}^1 . The first order 2-particle density matrix is then computed by finite difference

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