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σ -SCF: A direct energy-targeting method to mean-field excited states

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The mean-field solutions of electronic excited states are much less accessible than ground state (e.g., Hartree-Fock) solutions. Energy-based optimization methods for excited states, like Δ -SCF (self-consistent field), tend to fall into the lowest solution consistent with a given symmetry—a problem known as “variational collapse.” In this work, we combine the ideas of direct energy-targeting and variance-based optimization in order to describe excited states at the mean-field level. The resulting method, σ -SCF, has several advantages. First, it allows one to target any desired excited state by specifying a single parameter: a guess of the energy of that state. It can therefore, in principle, find *all* excited states. Second, it avoids variational collapse by using a variance-based, unconstrained local minimization. As a consequence, all states—ground or excited—are treated on an equal footing. Third, it provides an alternate approach to locate Δ -SCF solutions that are otherwise hardly accessible by the usual non-aufbau configuration initial guess. We present results for this new method for small atoms (He, Be) and molecules (H_2 , HF). We find that σ -SCF is very effective at locating excited states, including individual, high energy excitations within a dense manifold of excited states. Like all single determinant methods, σ -SCF shows prominent spin-symmetry breaking for open shell states and our results suggest that this method could be further improved with spin projection. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5001262>

I. INTRODUCTION

Mean-field solutions to the time-independent Schrödinger equation are of significant physical importance for two reasons. Qualitatively, they offer an understandable physical picture of the system’s electronic structure. Quantitatively, they serve as a starting point for correlated methods that hierarchically improve accuracy. For example, the combination of the Hartree-Fock (HF) approximation^{1,2} with post-Hartree-Fock methods^{3–8} is a triumph of quantum chemistry for electronic ground states: well-developed algorithms and user-friendly packages nowadays make *ab initio* calculation of the ground state accessible to anyone with a moderate personal computer.

Many excited state methods built atop ground state mean-field references have been developed. Single-reference linear response-based methods, such as CIS (configuration interaction singles^{9,10}), TDHF (time-dependent Hartree-Fock^{11,12}), and TDDFT (time-dependent density functional theory^{13–16}), have relatively modest computational scaling and are capable of giving qualitative—and sometimes even quantitative—predictions for low-energy valence excited states. However, these methods are very sensitive to the quality of the reference state (usually, the mean-field ground state) and therefore will break down when the reference is not a good approximation. Multi-reference (MR) wavefunction-based approaches, such as MRCI,¹⁷ MCSCF (multi-configurational self-consistent field^{18–20}), and CASPT2 (complete active space

perturbation theory of second order^{21–24}), as well as equation-of-motion^{25–28} and linear response^{29–32} coupled cluster theories (EOM-CC and LR-CC), are in principle able to offer great accuracy. However, these suffer from being computationally expensive and hence are limited for smaller molecules and/or moderate-sized basis set.

Another approach is to describe the excited state at the mean-field level (which may later be improved by the aforementioned correlated methods). Following this line, Δ -SCF,^{33–35} a direct generalization of the ground state Hartree-Fock method, has been developed. In this method, excited states are found using a non-aufbau electronic configuration generated by swapping occupied and virtual ground-state orbitals and then minimizing the energy. Unfortunately, this conceptually straightforward method is plagued by a severe numerical problem: the order of orbitals can change during the orbital relaxation, making it difficult to converge to a specific state. This deficiency arises from the fact that optimizing the energy of a non-aufbau single-determinantal wavefunction leads to a numerically unfavorable saddle point optimization in the Hilbert space. Gilbert *et al.*³⁶ partially alleviated this limitation by introducing the so-called maximum overlap method (MOM) in order to track a specific non-aufbau occupation throughout the self-consistent field (SCF) procedure. Despite its success, strong dependence on a good initial guess still mandates expertise.

Generally speaking, all energy-based minimization schemes suffer from the “variational collapse” problem,³⁷ in which variational optimization tends to find the lowest-energy solution of a given symmetry. This problem is fatal for our purpose of developing an excited state method and

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thus must be avoided. One cure to this is the so-called SCF metadynamics developed by Thom and Head-Gordon,³⁸ which adds biasing potentials to “fill in” minima in electronic wave function space that have already been found, thus avoiding the solutions being trapped in any one well. They also demonstrated that SCF solutions located in this way might serve as a quasidiabatic basis for NOCI (nonorthogonal configuration interaction^{39–41}) to produce adiabatic states.⁴⁰

Noting that excited states are local minima of energy variance, another possible proposal to avoid the variational collapse is to minimize variance instead of energy. Moreover, the exact lower bound of variance is known (i.e., zero), and hence the variance serves as an estimate of the quality of an approximate wavefunction. This idea was first proposed by Weinstein⁴² in 1934 and suggested by Bartlett *et al.*⁴³ one year later who performed the first calculation on helium. Then many numerical experiments were conducted by Frost and co-workers^{44–48} as well as Conroy^{49–51} to optimize trial wavefunctions in a minimized-variance style. Decades later, this scheme was introduced by Coldwell⁵² and Umrigar *et al.*⁵³ into the community of variational Monte Carlo (VMC) researchers, where it has since become popular.^{54–58}

The variance criterion transforms the Hilbert space landscape into a series of local minima, each corresponding to an electronic state. Thus, we need a method to target a desired state’s local minimum. In this work, we propose a direct energy-targeting functional $W[\Psi](\omega)$ [Eq. (1)] that can do both: (i) its global minimum in Hilbert space is an energy eigenstate whose energy is *closest* to ω —a guess of the energy of that state—and (ii) it reduces to the energy variance at the solution (i.e., when $\omega = \langle \Psi | \hat{H} | \Psi \rangle$). Thus the desired state targeted by ω can be obtained through a variance minimization after a preliminary energy-targeting calculation.

This paper is organized as follows. Section II is the theory section where we introduce the details of the mathematical formalism of σ -SCF and comment on the physical meaning of the solutions and computational scaling. In Sec. III, we give the computational details. In Sec. IV, we examine the quality of excited state σ -SCF solutions. We compare dissociation curves of several diatomic molecules and vertical excitation energies of some small atoms obtained by σ -SCF against other mean-field (i.e., Δ -SCF and CIS) or correlated (FCI) methods. In Sec. V, we examine properties of ground state σ -SCF solutions. We find that variance minimized solutions (σ -SCF) and energy minimized solutions (HF or Δ -SCF) have different behaviors at symmetry-breaking point. Then in Sec. VI, we discuss this distinction along with several other properties of σ -SCF. Finally, in Sec. VII, we conclude this work by pointing out several potential future directions.

II. THEORY

A. The direct energy-targeting function

Consider the following functional,⁴²

$$W[\Psi](\omega) \equiv \langle \Psi | (\omega - \hat{H})^2 | \Psi \rangle, \quad (1)$$

where Ψ is an arbitrary, fermionic, normalized wavefunction. By expanding $|\Psi\rangle$ in the eigenbasis, i.e., $|\Psi\rangle = \sum_n c_n |n\rangle$, one can easily prove a lemma similar to the Ritz-Schrödinger variational principle,⁵⁹

$$\begin{aligned} W[\Psi](\omega) &= \sum_n |c_n|^2 (E_n - \omega)^2 \\ &\geq (E_m - \omega)^2 \sum_n |c_n|^2 = (E_m - \omega)^2, \end{aligned} \quad (2)$$

where E_m is the energy level *closest* to ω in the ordered energy spectrum, i.e., $(E_m - \omega)^2 \leq (E_n - \omega)^2$ for all n . If non-degenerate, the equality holds if and only if $c_n = \delta_{nm}$ and hence the global minimum of $W[\Psi](\omega)$ in the Hilbert space is exactly $|m\rangle$. For the case of degeneracy, minimizing $W[\Psi](\omega)$ leads to a linear combination of states with energy E_m . More explicitly, we define an energy-targeting function

$$\Omega(\omega) \equiv \min_{\Psi} W[\Psi](\omega), \text{ subject to } \langle \Psi | \Psi \rangle = 1, \quad (3)$$

with the argument of the minimum denoted by $\Psi(\omega)$. Lemma (2) suggests that $\Omega(\omega)$ is composed of a series of overlapping parabolas centered on $\{E_n\}$. Alternatively, one can see this by applying the Hellmann-Feynman theorem^{60,61} to $\Omega(\omega)$,

$$\frac{\partial \Omega}{\partial \omega} = 2(\omega - \langle \hat{H} \rangle), \quad (4)$$

and hence a stationary point is given by $\omega = \langle \hat{H} \rangle$, where $\langle \cdots \rangle$ is an abbreviation of $\langle \Psi | \cdots | \Psi \rangle$. Thus $\Omega(\omega)$ reduces at its minimum to the energy variance, which is zero since no constraints on Ψ have been imposed. On the other hand, the energy as a function of ω ,

$$E(\omega) \equiv \langle \Psi(\omega) | \hat{H} | \Psi(\omega) \rangle, \quad (5)$$

consists of a series of step functions whose plateaus form a one-to-one mapping with the energy levels.

B. Connection to the variance-based minimization

In the mean-field level, where Ψ is further restricted to be a single Slater determinant Φ , the picture above requires modifications. As an illustrative example, we perform the energy-targeting calculation [Eq. (3)] in the mean-field level (see Sec. II C for detailed algorithm) for the H_2 molecule with a double- ζ basis set (Fig. 1). The results differ from the

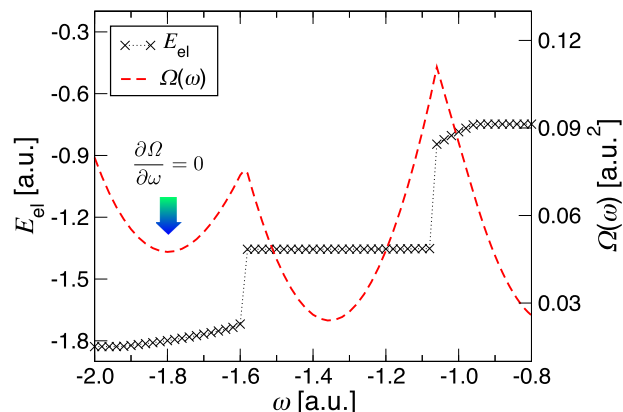


FIG. 1. Variation of $E(\omega)$ (black crosses) and $\Omega(\omega)$ (red dashed curves) with respect to ω in the mean-field level for 3-21G H_2 with bond length 0.75 Å.

exact picture in two ways. First, the local minima of $\mathcal{Q}(\omega)$ are no longer zeros due to the mean-field nature of $\Phi(\omega)$. Second, $E(\omega)$ is not strictly flat any more on each plateau, which weakens the power of lemma (2) since one has to further specify which point of $E(\omega)$ represents the energy of the desired state. Fortunately, the Hellmann-Feynman theorem [Eq. (4)] still guarantees that each local minimum of $\mathcal{Q}(\omega)$ (see the blue arrow in Fig. 1) corresponds to a mean-field solution. Thus one only needs a (mean-field) variance minimization, i.e.,

$$\sigma_H^2 = \min_{\Phi} S[\Phi], \text{ subject to } \langle \Phi | \Phi \rangle = 1, \quad (6)$$

after the energy-targeting calculation, where the energy variance functional is defined by

$$S[\Phi] \equiv W[\Phi](\omega)|_{\omega=\langle \hat{H} \rangle} = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2. \quad (7)$$

Note that although ansatz (6) has no dependence on ω , the energy-targeting information is retained as long as $\Phi(\omega)$ is used as initial guess for the subsequent variance minimization. One advantage is that this ω -free nature promises a unique, well-defined solution.

Up to this point, the formalism is general to any fermionic, mean-field system. In Sec. II C, we further confine our discussion to molecular systems. A two-step SCF algorithm, i.e., σ -SCF, is proposed accordingly.

C. The σ -SCF method

Consider a molecule with N electrons, whose electronic Hamiltonian in a chosen basis set $\{\phi_\mu\}$ can be written as

$$\hat{H} = \sum_s \sum_{\mu\nu} h_{\mu\nu} c_{\mu s}^\dagger c_{\nu s} + \frac{1}{2} \sum_{st} \sum_{\mu\nu\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle c_{\mu s}^\dagger c_{\nu t}^\dagger c_{\sigma t} c_{\lambda s}, \quad (8)$$

where K is the number of basis functions, s and t label electron spins, $h_{\mu\nu}$ and $\langle \mu\nu | \lambda\sigma \rangle$ are the usual one- and two-electron (in $\langle 12 | 12 \rangle$ order) integrals (TEIs), and $c_{\mu s}^\dagger$ creates one electron in ϕ_μ with spin s while $c_{\mu s}$ annihilates. For molecular systems, the basis set usually consists of atom-centered Gaussian functions or atomic orbitals (AOs). In the following derivation, unless otherwise specified, an orthonormal basis set is assumed for the sake of convenience. The aforementioned, non-orthogonal AOs can be orthogonalized readily using any convenient orthogonalization methods (e.g., the symmetric orthogonalization¹).

The mean-field electronic energy is a functional of one-electron reduced density matrices, i.e.,

$$E_{\text{el}}[\{P^s\}] = \frac{1}{2} \sum_s \sum_{\mu\nu} P_{\nu\mu}^s (h_{\mu\nu} + F_{\mu\nu}^s[\{P^s\}]), \quad (9)$$

where the Fock matrix for spin s is

$$F_{\mu\nu}^s[\{P^s\}] = h_{\mu\nu} + \sum_{\lambda\sigma} \left[\sum_t P_{\lambda\sigma}^t \langle \mu\sigma | \nu\lambda \rangle - P_{\lambda\sigma}^s \langle \mu\sigma | \lambda\nu \rangle \right]. \quad (10)$$

In Hartree-Fock, the energy functional [Eq. (9)] is minimized in an iterative manner, i.e., the self-consistent field (SCF) method. For comparison to the algorithm we propose in this paper, we first outline the SCF method for Hartree-Fock.¹ At first a trial density matrix P_0 is used to construct an initial Fock matrix, which is then diagonalized to give the coefficient matrix C for Hartree-Fock molecular orbitals (MO) $\{\psi_p\}$ spanned by $\{\phi_\mu\}$. Then a new density matrix is generated via the first N columns of C , i.e., $P = C\rho C^\dagger$, where ρ is a projection matrix to the N occupied orbitals. The above steps are repeated until self-consistency is reached. Several techniques including DIIS (direct inversion of iterative space⁶²) and RCA (relaxed constraint approximation⁶³⁻⁶⁵) can be used to accelerate the convergence.

To generalize the above algorithm, we note that the Fock matrix defined in Eq. (10) can also be viewed as a functional derivative of energy with respect to density matrix, i.e.,

$$F_{\mu\nu}^s[\{P^s\}] = \frac{\partial E_{\text{el}}[\{P^s\}]}{\partial P_{\mu\nu}^s}. \quad (11)$$

For the purposes of minimizing $W(\omega)$ and S , we thus define two generalized Fock matrices

$$f_{\mu\nu}^s[\{P^s\}](\omega) \equiv \frac{\partial W[\{P^s\}](\omega)}{\partial P_{\mu\nu}^s}, \quad (12)$$

$$\mathcal{F}_{\mu\nu}^s[\{P^s\}] \equiv \frac{\partial S[\{P^s\}]}{\partial P_{\mu\nu}^s}, \quad (13)$$

for energy-targeting and variance minimization, respectively. We defer the expressions of f and \mathcal{F} to Sec. II D. By replacing F with them, it is straightforward to generalize the above SCF algorithm for our purposes. Thus, the σ -SCF algorithm for a state targeted by ω can be articulated as follows:

1. Choose an appropriate value for ω .
2. Self-consistently perform the energy-targeting calculation with f the Fock matrix; obtain the solution $\Phi(\omega)$ in terms of $P(\omega)$.
3. Using $P(\omega)$ generated above as initial guess, self-consistently perform the variance minimization with \mathcal{F} the Fock matrix.

This process is also schematically summarized in Fig. 2.

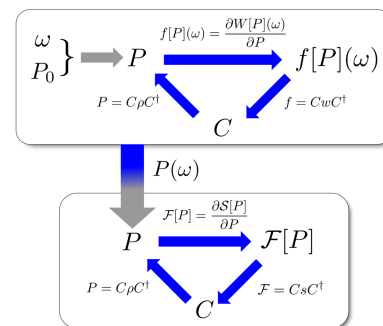


FIG. 2. Schematic illustration of the σ -SCF algorithm. The energy-targeting optimization (top) offers $P(\omega)$ as an initial guess to a variance minimization (bottom). ρ is the projection matrix onto occupied orbitals. s is the eigenvalue matrix of \mathcal{F} whose physical meaning will be discussed in Sec. II E.

D. Generalized Fock matrices

In this section, we derive expressions for the generalized Fock matrices defined in Eqs. (12) and (13). We first note that since $W[\Phi](\omega)$ and $S[\Phi]$ are related,

$$W[\Phi](\omega) = S[\Phi] + (\omega - \langle \hat{H} \rangle)^2, \quad (14)$$

so are f and \mathcal{F} . It is thus enough to evaluate one set of them, e.g., S and \mathcal{F} . In MO basis, the energy variance $S[\Phi]$ can be readily calculated by applying the Slater-Condon rule^{1,66} after a resolution of identity

$$S[\Phi] = \sum_s \sum_{i,a} |F_{ia}^s|^2 + \frac{1}{2} \sum_{st} \sum_{i,a} \sum_{j,b} |\langle ij || ab \rangle|^2, \quad (15)$$

where i, j, \dots and a, b, \dots label occupied and virtual MOs, respectively; $\langle ij || ab \rangle$ are anti-symmetrized TEIs. Equation (15) can be transformed back into the AO basis, i.e.,

$$\begin{aligned} S[\{P^s\}] &= \sum_s \text{Tr} F^s P^s F^s Q^s \\ &+ \frac{1}{2} \sum_{st} \sum_{\substack{\mu\nu\lambda\sigma \\ \mu'\nu'\lambda'\sigma'}}^K \langle \mu\nu || \lambda\sigma \rangle \langle \mu'\nu' || \lambda'\sigma' \rangle \\ &\times P_{\mu\mu'}^s P_{\nu\nu'}^t Q_{\lambda\lambda'}^s Q_{\sigma\sigma'}^t, \end{aligned} \quad (16)$$

where $Q^s = I - P^s$. Combining this with Eq. (13), we have

$$\begin{aligned} \mathcal{F}_{\mu\mu'}^s[\{P^s\}] &= [F^s(Q^s - P^s)F^s]_{\mu\mu'} \\ &+ \sum_t \text{Tr} X^{\mu\mu'} P^t F^t Q^t + \text{Tr} F^t P^t X^{\mu\mu'} Q^t \\ &- \text{Tr} \tilde{X}^{\mu\mu'} P^s F^s Q^s + \text{Tr} F^s P^s \tilde{X}^{\mu\mu'} Q^s \\ &+ \sum_t \sum_{\substack{\nu\lambda\sigma \\ \nu'\lambda'\sigma'}} \langle \mu\nu || \lambda\sigma \rangle \langle \lambda'\sigma' || \mu'\nu' \rangle \\ &\times [P_{\nu\nu'}^t Q_{\lambda\lambda'}^s Q_{\sigma\sigma'}^t - Q_{\nu\nu'}^t P_{\lambda\lambda'}^s P_{\sigma\sigma'}^t], \end{aligned} \quad (17)$$

where $X^{\mu\mu'}$ and $\tilde{X}^{\mu\mu'}$ are both K -by- K matrices derived from the TEI tensor, i.e., $(X^{\mu\mu'})_{\lambda\sigma} = \langle \mu\lambda || \mu'\sigma \rangle$ and $(\tilde{X}^{\mu\mu'})_{\lambda\sigma} = \langle \mu\lambda || \sigma\mu' \rangle$. Formulae for $W[\{P^s\}](\omega)$ and $f[\{P^s\}]$ can be derived using the relation in Eq. (14).

Similar to Hartree-Fock, the σ -SCF method is size-consistent, i.e., the energy of two monomers separated by a (infinitely) large distance is twice the energy of that monomer. The proof is straightforward: since both the atomic integrals and the density matrix elements vanish if they involve atomic orbitals from different monomers, \mathcal{F} is block-diagonalized and the off-diagonal blocks, which represent interaction between two monomers, must vanish. We also note that besides energy, the variance follows the same linear addition rule. These conclusions are numerically verified and illustrated in the [supplementary material](#) (Table S1).

E. Orbital variance

From a mathematical point of view, the SCF algorithm we introduced above is to iteratively solve the following non-linear, generalized eigenvalue equation (ignoring spin for simplicity)

$$\mathcal{F}[P]c_n = S c_n s_n, \quad (18)$$

where S is the overlap matrix for the basis set and c_n is the n th column in C . The eigenvalues $\{s_n\}$ have the unit of energy square and are termed “orbital variance” in analogy to the concept of “orbital energy” in Hartree-Fock. The explicit expressions of σ -SCF orbital variance can be obtained by transforming Eq. (17) into the MO basis and take the diagonal elements. Unfortunately, unlike its energy counterpart which can be classically interpreted as the energy for a single electron moving in an averaged Coulomb repulsion field exerted by other electrons, it is unclear how to assign a simple physical meaning to each of the terms in the orbital variance expression due to its complex form.

Some insights, however, can be gained from numerical examinations, which suggest that s_n are always negative for occupied orbitals ($n \leq N$) and positive for unoccupied ones ($n > N$), if the aufbau principle is observed. In fact, similar to the existence theorem for Hartree-Fock aufbau solutions given by Lions,⁶⁷ one may argue that solutions obtained by occupying N canonical orbitals with *lowest orbital variance* (i.e., aufbau configurations in terms of orbital variance) do exist. This can also be understood in terms of the Janak theorem,⁶⁸ i.e., the total variance would increase by either attaching an electron on a virtual orbital or detaching one from an occupied orbital.

F. Computational scaling

Before moving on, we give a note on the computational scaling of σ -SCF. Similar to Hartree-Fock, the most time-consuming step in each self-consistent iteration is the construction of \mathcal{F} and f , whose formal scaling is $O(K^5)$ as is apparent in Eq. (15). This scaling is slightly higher than that of Hartree-Fock [$O(K^4)$] but lower than most correlated excited state methods. It is possible to reduce this scaling by taking advantage of the sparsity of the TEI tensor.

III. COMPUTATIONAL DETAILS

The σ -SCF algorithm described above was implemented using C++ with the linear algebra library Eigen.⁶⁹ All atomic integrals (e.g., $h_{\mu\nu}$, $\langle \mu\nu || \lambda\sigma \rangle$, etc.), as well as results from CIS and Δ -SCF, are generated by Q-Chem 4.3.⁷⁰ For CIS, the unrestricted Hartree-Fock (UHF) ground state is used as the reference state. For Δ -SCF, the initial guess is obtained by either performing a preliminary ground state calculation and then pushing electrons from occupied to virtual orbitals³⁶ or taking the corresponding σ -SCF solution. Unless otherwise specified, MOM is used to keep track of a desired state during the SCF procedure. For systems we consider in this work, the FCI solutions are always available and thus used as benchmark. For σ -SCF, in order to stay on a single PES and avoid state-hopping, the solution begins with an ansatz from an available solution with the closest geometry. For whatever spin multiplicity, the aufbau configuration consistent with it is employed. Finally, a symmetry-breaking initial guess is always used. For some cases, the spin-symmetry is recovered after achieving self-consistency, which leads to the spin-restricted σ -SCF (R σ -SCF) solutions. Otherwise, we have spin-unrestricted solutions (U σ -SCF).

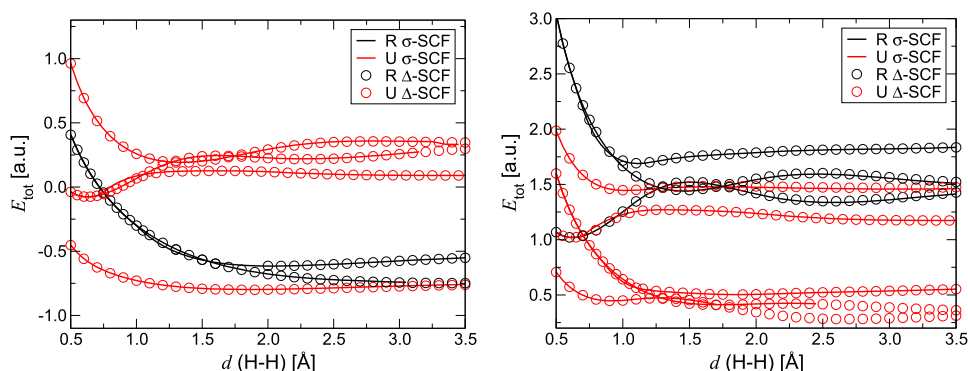


FIG. 3. The excited states energy ($M_s = 0$) of 3-21G H_2 along bond dissociation, predicted by σ -SCF (solid curves) and Δ -SCF (circles). Black and red are used for spin-restricted and unrestricted solutions, respectively.

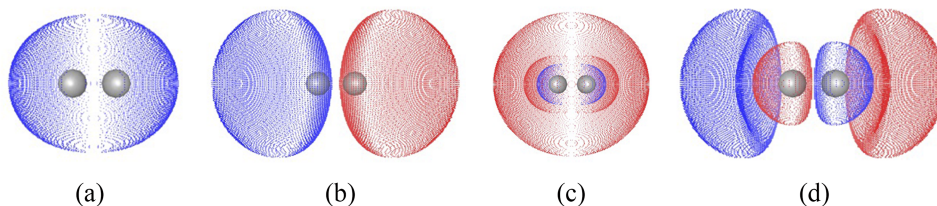


FIG. 4. Isosurface plot (cutoff: 0.05) of the four typical σ -SCF molecular orbitals for 3-21G H_2 at equilibrium geometry.

IV. EXCITED STATES

A. 3-21G H_2

The first example is the hydrogen molecule in a double- ζ basis set 3-21G.⁷¹ In Fig. 3, the dissociation curves predicted by σ -SCF and Δ -SCF are compared for all excited states found ($M_s = 0$ only). Overall, the match between these two methods is not only qualitative but also quantitative: for every Δ -SCF solution, we can find a σ -SCF counterpart which follows the former closely, though one is stationary in energy and the other in energy variance. We also point out that beyond some bond length, the latter has convergence issue due to lack of flexibility in the selected basis set.⁵⁶

Another interesting aspect to explore is the profile of the mean-field wavefunctions for excited states. According to the chemical bonding theory, 3-21G, which has two s orbitals on each hydrogen atom, can give rise to four σ orbitals if the C_2 symmetry is preserved. This classical picture is confirmed by the isosurface plots of HOMOs (highest occupied molecular orbitals) for σ -SCF excited states (see Fig. S1 of the [supplementary material](#)). As expected, there are four typical molecular orbitals (Fig. 4), which resemble in shape the bonding/anti-bonding σ orbitals formed by hydrogen's $1s$ and $2s$ atomic orbitals, respectively. We thus label them as σ_1/σ_1^* and σ_2/σ_2^* to reflect it.

In spite of the similarity, a closer scrutiny on Fig. 3 reveals that these two methods behave differently at the symmetry-breaking points. For example, $|\sigma_2, \sigma_1\rangle$ bifurcates into two branches at a bond length of 0.72 Å, while its Δ -SCF counterpart does at around 0.97 Å (Fig. 5). From the orbital isosurface plots (inset of Fig. 5), one can further specify that the symmetry being broken associated with these PES bifurcations is the C_2 spatial symmetry. Another interesting observation is that the broken-symmetry solution obtained by Δ -SCF is smooth for all bond lengths, while the σ -SCF one has a “kink” (i.e., discontinuous first-order derivative) right at the symmetry-breaking point. This phenomenon can be credited to an underlying

duality between energy and its variance and is discussed in detail in Sec. VI.

Before moving on to the next molecule, we compare our results with the benchmark, FCI. Gilbert *et al.* have demonstrated that the mean-field excited states (found by Δ -SCF with MOM) give relatively good vertical excitation energies.³⁶ Here, we show the qualitative profile of the whole mean-field Born-Oppenheimer PES. Our results are presented in Fig. 6, from which one can draw three observations: (i) overall, the mean-field solutions capture the qualitative shape of the exact solutions; (ii) mean-field solutions with broken symmetry (symmetries) predict the correct asymptotic behavior for PES, however, with a wrong wavefunction since the exact wavefunction should preserve those (spin and spatial) symmetries; (iii) by an elaborate selection of the mean-field states, one can form a one-to-one mapping between the mean-field and the exact solutions. (See Fig. S2 in the [supplementary material](#) for one such realization.) In other words, for this specific case, the selected σ -SCF solutions form a complete

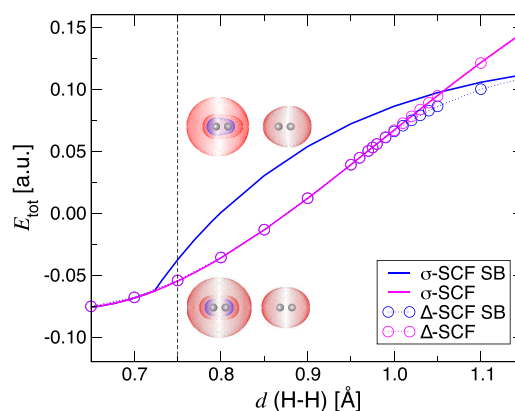


FIG. 5. A zoom-in view of the symmetry-breaking (SB) points for selected σ -SCF solutions of 3-21G H_2 and the corresponding Δ -SCF solutions. Inset: isosurface plots of HOMOs at the equilibrium geometry for the selected σ -SCF states.

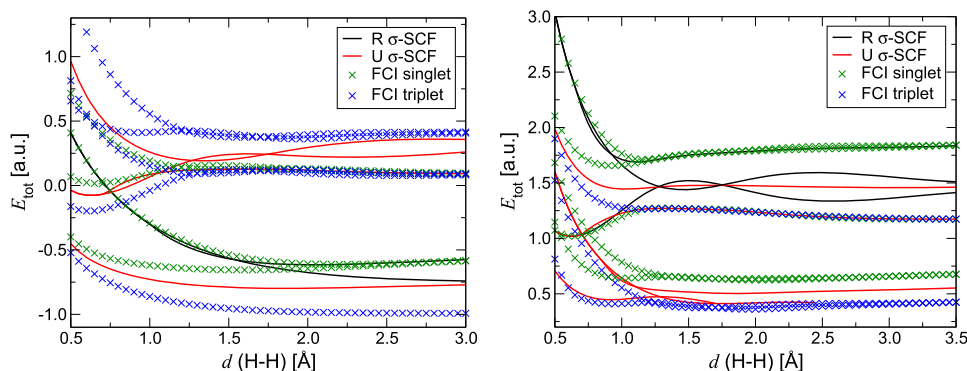


FIG. 6. The excited states energy ($M_s = 0$) of 3-21G H_2 along bond dissociation, predicted by σ -SCF (solid curves) and FCI (crosses).

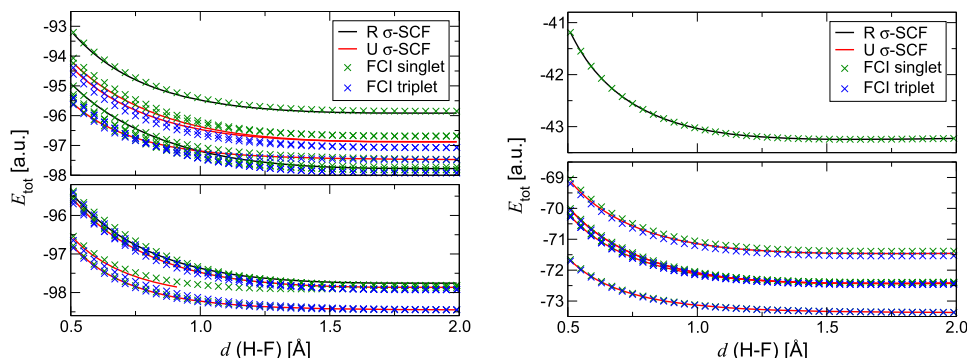


FIG. 7. The excited states energy ($M_s = 0$) of STO-3G HF along bond dissociation, predicted by σ -SCF (solid curves) and FCI (crosses).

basis for the CI space and can therefore be used in methods such as NOCI. We emphasize, however, that this completeness is only an empirical observation and might not hold true for larger basis sets. Nevertheless, in practice, there are usually a finite number of states that are of most interest within a certain energy window, and we will see in the following examples that σ -SCF does a good job in locating those states.

B. STO-3G HF

We then turn to an asymmetric linear molecule, hydrogen fluoride, in a minimal basis set STO-3G.⁷² As the system becomes larger, Δ -SCF starts to have difficulty in converging to some of the desired states while σ -SCF still works smoothly. In Fig. 7, we show the σ -SCF excited-state ($M_s = 0$) dissociation curves and compare them with the benchmark results. These mean-field excited states have similar properties as those of H_2 (Fig. 6) and manage to capture the qualitative behavior of the FCI PESs. Of special interest is the good description of the high-energy Rydberg-like state (top-right panel in Fig. 7). Population analysis suggests that this state corresponds to an excitation of the fluoride $1s$ core electrons to the valence shell.

In terms of number of states, σ -SCF again locates all states of interest for such a small-sized basis set. One can check this, for instance, using solutions within a specific energy window shown in the bottom-right panel of Fig. 7. There are four U σ -SCF dissociation curves therein, each lying between one singlet and one triplet FCI curves. Thus the total number of mean-field solutions matches that of FCI for this energy range. For details on how these states are related, see the [supplementary material](#) (Table S2).

C. 6-311G He

The third example is the helium atom in a triple- ζ basis set 6-311G.⁷³ There are nine determinants with $M_s = 0$ and six with $M_s = \pm 1$ associated with this basis set. σ -SCF manages to locate all these states as tabulated in Table I, along with the benchmark results for comparison. Note that there are three doubly degenerate (by spin symmetry), spin-contaminated $M_s = 0$ solutions (state 2/3, 5/6 and 7/8), each of which is split into one singlet and one triplet in FCI. For these states, relatively large deviations from the exact energies are observed due to the multi-configurational nature. However, the fact that $\langle \hat{S}^2 \rangle \approx 1$ indicates that they are all 1:1 mixtures of singlet and triplet states. Thus we propose the following spin-purification

TABLE I. Energy levels of 6-311G He (unit: a.u.) predicted by σ -SCF and FCI. For spin-contaminated states, errors are calculated using E^{SP} .

M_s	State	σ -SCF			FCI		Error
		E	$\langle \hat{S}^2 \rangle$	E^{SP}	E	$\langle \hat{S}^2 \rangle$	
0	1	-2.860	0		-2.876	0	0.017
	2	-1.651	0.992	-1.791	-1.791	2	0
	3	-1.651	0.992	-1.511	-1.525	0	0.014
	4	-0.163	0		-0.162	0	-0.001
	5	3.399	0.999	3.202	3.202	2	0
	6	3.399	0.999	3.596	3.572	0	0.024
	7	4.576	0.997	4.442	4.442	2	0
	8	4.576	0.997	4.709	4.762	0	0.053
	9	9.968	0		9.977	0	-0.009
± 1	1	-1.791	2		-1.791	2	0
	2	3.202	2		3.202	2	0
	3	4.442	2		4.442	2	0

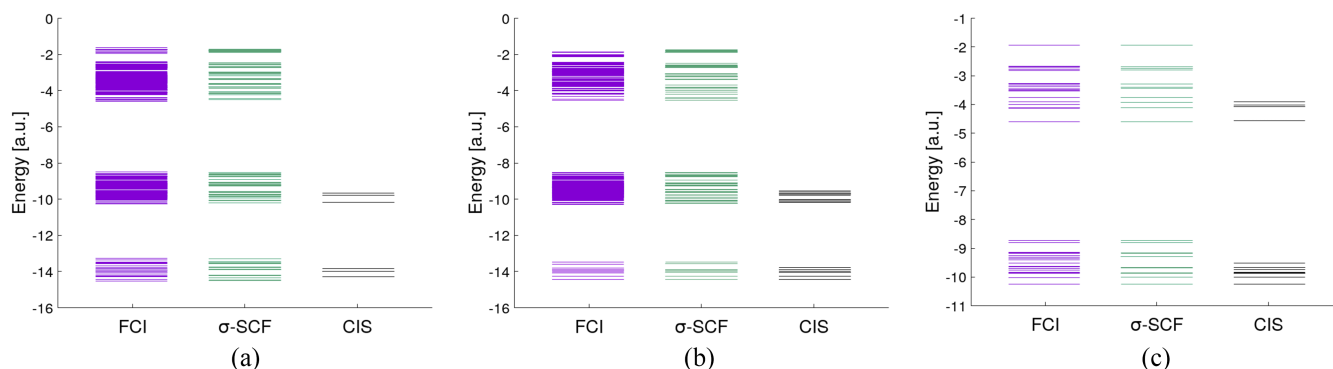


FIG. 8. Electronic energy spectrum for 3-21G Be predicted by σ -SCF. CIS and FCI results are also included for comparison.

(SP) procedure,

$$E_{\sigma\text{-SCF}}^{\text{SP}} = 2E_{\sigma\text{-SCF}}^{M_s=0} - E_{\sigma\text{-SCF}}^{M_s=\pm 1}, \quad (19)$$

to remove the triplet components and obtain a spin-purified “singlet” energy for σ -SCF. These results are also listed in Table I, from which one can see that the SP procedure does give rise to reasonable energies. Besides, other σ -SCF solutions (which are either pure singlet or triplet states for the special case of He) are in fact of good precision. The error reduces from the singlet ground state to excited states, as the latter have spatially more extensive orbitals for electrons to avoid each other. States with $M_s = \pm 1$ are thus expected to be even more accurate since correlations between parallel spins have already been accounted for in the mean-field level.

D. 3-21G Be

In the example above, one might expect Δ -SCF to have an equally good performance for locating excited states since the size of the system (i.e., number of electrons and size of basis set) is very small. As a more severe check, we calculate the whole energy spectrum for beryllium with the 3-21G basis set.⁷¹ Through occupying all 18 spin orbitals with 4 electrons, 1296, 1512, and 252 determinants are generated with $M_s = 0$, ± 1 , and ± 2 , respectively. Such a large number of states make the energy spectrum nearly a continuum, and thus we take a relatively small step length (0.03 a.u.) for the ω scanning to ensure that σ -SCF finds as many solutions as possible. The results are shown in Fig. 8, along with CIS and FCI solutions for comparison. Again the σ -SCF method does a good job in reproducing most qualitative features of the FCI spectrum for all spin multiplicities. CIS, on the other hand, captures only the singly excited states due to its linear response nature and hence has a much sparse spectrum. For this case and systems of even larger size, locating *all* σ -SCF solutions is numerically challenging. Nevertheless, as mentioned above, in practice, only a small number of states within a specific energy window are relevant in methods such as NOCI. The dense profile of the σ -SCF spectrum is therefore an indication that it can capture such relevant states for a relatively wide range of energy.

V. GROUND STATES

Although the σ -SCF method was developed for excited states, it is also interesting to see how it behaves for the ground

state, especially for the purpose of comparing the energy- (i.e., Hartree-Fock) and the variance-based minimization schemes.

We perform σ -SCF calculations for the ground state dissociation curves of 3-21G H_2 . The obtained PESs are illustrated in Fig. 9, along with the Hartree-Fock and FCI results for comparison. For the spin-restricted case, both σ -SCF and Hartree-Fock predict similar PESs which nearly overlap each other. Closer scrutiny, however, reveals that the RHF solution is lower in energy and higher in variance (inset panel of Fig. 9), which is consistent with the quantity being minimized in each method. If the restricted-spin constraint is relaxed, both solutions break the spin symmetry and generate a spin-unrestricted branch. They differ, however, in the following two aspects. First, the bifurcation of the R σ -SCF solution comes earlier than that of RHF, with bond length around 0.67 Å and 1.17 Å, respectively. Second, the bifurcation is smooth for the RHF PES (i.e., the corresponding UHF solution has a continuous first-order derivative at the symmetry-breaking point), while exhibiting a discontinuous derivative for the σ -SCF counterpart, and the opposite is true for the energy variance. These results are a special case of what we have observed at the symmetry-breaking points for excited states. Despite the distinctions, these two unrestricted solutions do have the same asymptotic behavior for both energy and energy variance (which also overlap the trend of the FCI solution, for reasons we have already discussed in Sec. IV A).

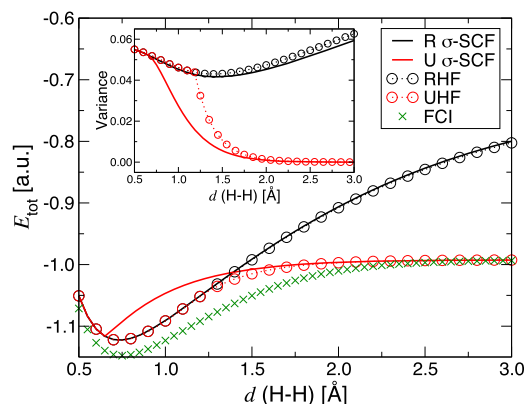


FIG. 9. Ground state energy of 3-21G H_2 along bond dissociation, predicted by σ -SCF (solid curves), Hartree-Fock (circles), and FCI (crosses). Inset panel is the corresponding energy variance.

VI. DISCUSSION

- (1) *Reduced dimension of targeting space.* In terms of targeting excited states, the Δ -SCF method uses non-aufbau determinantal wavefunctions and is thus a global state-searching algorithm whose targeting space is the whole Hilbert space consisting of Slater determinants. Due to its high dimension, this targeting space becomes more difficult to search as the system size grows. The σ -SCF ansatz, on the other hand, collapses all degrees of freedom down to a single parameter, namely ω , which is a significant dimension reduction of the targeting space and renders it numerically advantageous. In fact, all the spatial symmetry-broken Δ -SCF solutions for 3-21G H_2 shown in Fig. 3 are obtained using their σ -SCF counterparts as initial guesses. These states are otherwise difficult to locate even when the MOM is used.

Another implication of this dimension reduction is that each excited state corresponds to a local minimum in variance, so it is possible to use a bracketing scheme to efficiently find all excited states in a given energy window.⁷⁴ The most straightforward way to achieve this is to simply scan ω in that energy range with a step length less than the minimum separation between two neighboring levels in the ordered energy spectrum, which is exactly what we did for the calculation of Be atom (Sec. IV D).

- (2) *Variance- versus energy-based optimization.* The primary motivation for us to assume a variance-based scheme is to avoid variational collapse. A significant point to address is how the accuracy of a variance-based approach compares to an energy-based approach for mean-field solutions. Many studies related to this issue have been done by the quantum Monte Carlo practitioners,^{75–78} who concluded that for the ground state, the wavefunctions with minimized variance are either equal to or slightly worse than those with minimized energy in quality, especially when the trial wavefunction is not flexible enough (For example, one can check that no variance minima exist for a hydrogen atom with only one s -type Gaussian orbital.⁵⁶).

The comparison we made in Sec. IV A between σ -SCF and Δ -SCF suggests three features of mean-field wavefunctions of minimized variance for excited states. First of all, the basis set flexibility problem occurs for excited states, too (e.g., Fig. 3 right panel and Fig. 7 left panel). Second, they have a different behavior at the symmetry-breaking point compared with solutions of optimized energy (i.e., early symmetry breaking and a kink on PES). Third, they are always slightly higher in energy than solutions of optimized energy, which is not a trivial observation since for excited states the latter are generally not minima of energy. Nevertheless, for geometries away from the symmetry-breaking points, solutions derived from these two optimization schemes have very similar properties such as energy and variance.

- (3) *Direct energy-targeting.* Besides the functional $W[\Psi](\omega)$ [Eq. (3)] used in this work, another way to

achieve direct energy-targeting has been suggested by Choi *et al.*⁷⁹ in the 1970s

$$\tilde{Q}[\Psi](\omega) = \frac{\langle \Psi | (\omega - \hat{H}) | \Psi \rangle}{\langle \Psi | (\omega - \hat{H})^2 | \Psi \rangle}, \quad (20)$$

whose global minimum in Hilbert space is an eigenstate of \hat{H} with energy *immediately above* ω in the ordered energy spectrum. Recently Zhao and Neuscamman⁸⁰ optimized $\tilde{Q}[\Psi](\omega)$ with VMC and obtained relatively accurate excitation energies for small molecules. While it was successful with VMC, $\tilde{Q}[\Psi](\omega)$ is hard to optimize in a mean-field manner due to the functional form.

- (4) *Energy-variance duality and symmetry breaking.* One major distinction between variance- and energy-optimized solutions lies in their behavior at the symmetry-breaking point, where both the former's PES and the latter's variance-bond length function have a discontinuous first-order derivative. Let us consider some nuclear coordinate X . Then for the expectation value of a Hermitian operator \hat{A} , its X -derivative consists of two parts

$$\frac{\partial \langle \hat{A} \rangle}{\partial X} = \left\langle \frac{\partial \hat{A}}{\partial X} \right\rangle + \langle \hat{A} \rangle_X, \quad (21)$$

where the first term is the derivative of the operator and the second, the wavefunction, i.e.,

$$\langle \cdots \rangle_X \equiv \left\langle \frac{\partial \Psi}{\partial X} \middle| \cdots \middle| \Psi \right\rangle + \text{c.c.} \quad (22)$$

Thus, the X -derivatives of energy and its variance are

$$\frac{\partial E}{\partial X} = \left\langle \frac{\partial \hat{H}}{\partial X} \right\rangle + \langle \hat{H} \rangle_X \quad (23)$$

and

$$\frac{\partial \sigma_H^2}{\partial X} = \left\langle \left\{ \hat{H}, \frac{\partial \hat{H}}{\partial X} \right\} \right\rangle - 2E \left\langle \frac{\partial \hat{H}}{\partial X} \right\rangle + \langle \hat{H}^2 \rangle_X - 2E \langle \hat{H} \rangle_X, \quad (24)$$

respectively. From these expressions, we note that the discontinuity in the derivative of σ -SCF PES and Hartree-Fock energy variance must come from terms that involve derivatives of the wavefunction because all other terms consist of expectations over \hat{H} and its derivative $\partial \hat{H} / \partial X$ and are hence continuous for all bond length.

These two expressions can be related, if we notice that the second term in Eq. (21) vanishes when the Hellmann-Feynman theorem holds for $\langle \hat{A} \rangle$. This is the case for the energy variance of σ -SCF solutions. Thus Eq. (24) reduces to

$$\frac{\partial \sigma_H^2}{\partial X} = \left\langle \frac{\partial \hat{\sigma}_H^2}{\partial X} \right\rangle = \left\langle \left\{ \hat{H}, \frac{\partial \hat{H}}{\partial X} \right\} \right\rangle - 2E \left\langle \frac{\partial \hat{H}}{\partial X} \right\rangle, \quad (25)$$

where $\hat{\sigma}_H^2 \equiv (\hat{H} - E)^2$ and

$$\langle \hat{H}^2 \rangle_X = 2E \langle \hat{H} \rangle_X. \quad (26)$$

The identity above enables us to rewrite the energy derivative for σ -SCF as

$$\frac{\partial E}{\partial X} = \left\langle \frac{\partial \hat{H}}{\partial X} \right\rangle + \frac{1}{2E} \langle \hat{H}^2 \rangle_X. \quad (27)$$

Similarly for Hartree-Fock, the Hellmann-Feynman theorem holds for energy and indicates that $\langle \hat{H} \rangle_X$ vanishes. The derivative of energy variance thus takes the simple form

$$\frac{\partial \sigma_H^2}{\partial X} = \left\langle \frac{\partial \hat{H}^2}{\partial X} \right\rangle + \langle \hat{H}^2 \rangle_X. \quad (28)$$

These two equations closely resemble each other. The continuity of the same quantity, i.e., $\langle \hat{H}^2 \rangle_X$, controls the smoothness of both the σ -SCF PES and the Hartree-Fock variance-bond length function. This duality is somewhat harmful for σ -SCF since it leads to a discontinuity in the derivative of PES whenever there is a symmetry breaking.

VII. CONCLUDING REMARKS

In conclusion, we have introduced a new mean-field excited state method with direct energy-targeting based on variance-minimization. We demonstrated that by combining these two concepts, we not only avoid the variational collapse problem of energy-based methods but also locate desired excited states in an effective and controllable manner. Numerical examinations on first-row atoms and diatomic molecules suggest that solutions obtained in this way have similar properties compared to those located by energy-based methods such as Δ -SCF, though the former are numerically easier to locate even for systems of moderate size. The difference between these two types of solutions was found to be the positions of the symmetry-breaking points as well as the smoothness of the broken-symmetry solutions at those points. We showed that there is an underlying duality between energy and its variance, which makes the solution of optimized variance (energy) have discontinuity in the first-order derivative of energy (variance). A direct consequence of this duality is that the ground-state U σ -SCF PES is not smooth and hence would cause problems for molecular dynamics simulation. Nevertheless, as we have shown that whenever required, one can always use these solutions as initial guesses for methods like Δ -SCF to obtain smooth PESs.

In addition, we have shown that both the excited state PESs and the energy spectrum predicted by σ -SCF are qualitatively comparable to those obtained from the exact solution. Among them, three observations are of special interest. First, the behavior of the high-energy Rydberg-like state of hydrogen fluoride is well-described by σ -SCF. Second, energies of spin-contaminated solutions can be improved a lot by a simple spin-purification procedure. Third, after a proper choice of σ -SCF solutions, one can construct a well-defined non-orthogonal determinantal basis for the Hilbert space.

With these mean-field excited states in hand, there are several approaches to adding correlation and here we note a few. One straightforward modification is the spin-purification procedure discussed in Sec. IV C, which would not require additional computation. Additionally, σ -SCF solutions can be used in a Slater-Jastrow wavefunction and hence serve as an input for VMC and following DMC (diffusion Monte Carlo^{81,82}) calculations. This provides an alternate workflow to the VMC-based direct energy-targeting method proposed by Zhao and Neuscamman.⁸⁰ Moreover, the fact that σ -SCF

solutions can form a well-defined determinantal basis set indicates its potential application in NOCI calculations of excited states. Last but not least, the fact that σ -SCF solutions can be used as initial guesses for Δ -SCF calculations (especially the power to obtain previously hardly accessible solutions) might enable its application in the context of DFT.

While σ -SCF in its present form has a higher computational scaling compared to Δ -SCF, there are cases where the numerical robustness and stability may prove useful to locate excited states that are difficult to access in Δ -SCF or are completely unavailable in linear response methods such as CIS. We expect these properties will make σ -SCF useful for generating a complete basis set for correlated excited state methods, which generally have a higher computational scaling than σ -SCF, in any case.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for a complete plot of HOMO of all σ -SCF states for 3-21G H₂ and how σ -SCF solutions are related to FCI solutions.

ACKNOWLEDGMENTS

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