Configuration interaction combined with spin-projection for strongly correlated molecular electronic structures

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We introduce single and double particle-hole excitations in the recently revived spin-projected Hartree-Fock. Our motivation is to treat static correlation with spin-projection and recover the residual correlation, mostly dynamic in nature, with simple configuration interaction (CI). To this end, we present the Wick theorem for nonorthogonal determinants, which enables an efficient implementation in conjunction with the direct CI scheme. The proposed approach, termed ECISD, achieves a balanced treatment between dynamic and static correlations. To approximately account for the quadruple excitations, we also modify the well-known Davidson correction. We report our approaches yield surprisingly accurate potential curves for HF, H2O, N2, and a hydrogen lattice, compared to traditional single reference wave function methods at the same computational scaling as regular CI.

Despite the long elaboration of theoretical developments for electron correlation, an accurate black-box description of dynamic and static (strong) correlations yet remains unachieved. The difficulty comes from the fact that most multi-reference (MR) methods require to define an active space, where electrons are assumed to be strongly correlated. If such a space is not appropriately set up, one does not obtain a qualitatively correct zeroth order wave function and perturbation theory can suffer from intruder states. Introducing a larger active space to avoid this issue increases the computational cost exponentially, and thus its application has been limited to small systems.

Recently, many authors have vigorously tackled the strong correlation problem from different perspectives. Among them, projected Hartree-Fock (PHF) stands on symmetry-breaking and restoration in the mean-field picture, and delivers static correlations efficiently. Scuseria et al. have extended PHF to describe the residual dynamic correlations by sequentially updating and adding PHF wave functions based on approximate excited PHF states. Hence, the approach employs different orbitals for different configurations, and is commonly regarded as nonorthogonal configuration interaction (NOCI). The spirit behind NOCI is that the energy convergence with respect to the number of configurations is much faster than the orthogonal one. Unfortunately, the number of configurations required to achieve the chemical accuracy in NOCI increases exponentially with the system size, hampering its practical applications in part because it is hard to know when to terminate the CI expansion, which is crucial for a balanced treatment between different systems.

A more natural choice for CI basis is the “particle-hole” picture of excited determinants. While conceptually simple, it was considered that this canonical CI scheme would involve a very high cost due to the lack of simple Slater-Condon rule for the projected (nonorthogonal) Hamiltonian elements, whose evaluations thus were determined to be the most computationally demanding step. In this manuscript, however, we show that one can formulate the particle-hole CI in a manner quite similar to the regular direct CI scheme while retaining the same computational scaling.

Our wave function ansatz is therefore CI with singles and doubles (CISD) built from the broken-symmetry deformed state, which is explicitly projected to the correct symmetry-space with projection operator \( \hat{P} \),

\[
|\Psi\rangle = \hat{P} \left( c_0 |\Phi\rangle + \sum_{i} c_i^a |\Phi_i^a\rangle + \sum_{i,j,a,b} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \right),
\]

where \( |\Phi_i^a\rangle \) and \( |\Phi_{ij}^{ab}\rangle \) are singly and doubly excited determinants. Throughout this Communication, we will stick with the conventional orbital indices, where \( i,j,k,l \) represent occupied, \( a,b,c,d \) virtual, and \( p,q,r,s \) general orbitals. Also, we only consider the \( S^2 \)-symmetry in our projection because it is widely recognized as the most important symmetry for static correlation. \( \hat{P} \) is thus an exact spin-projector and removes all the spin-contaminants associated with broken symmetry determinants in the CI expansion, so that \( |\Psi\rangle \) is an eigenfunction of \( \hat{S}^2 \). Therefore, we will henceforth call this scheme spin-extended CISD (ECISD), in the philosophy of Löwdin’s spin-extended HF, which is also referred to as spin-projected unrestricted HF (SUHF) in the recent literature. Although ECISD employs orthogonal broken-symmetry determinants, it can be also considered a NOCI method with well-defined coordinates, \( \{ \hat{P}|\Phi\rangle, \hat{P}|\Phi_i^a\rangle, \hat{P}|\Phi_{ij}^{ab}\rangle \} \), and the basis is generically over-complete.

The residual correlation of ECISD, \( \Delta E_{SD} = E_{ECISD} - E_{SUHF} \), is given by

\[
\Delta E_{SD} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2)
\]

where \( \hat{H} = \hat{H} - E_{SUHF} \). As in regular CISD, one variationally minimizes \( \Delta E_{SD} \), resulting in the following equations for configuration coefficients \( c \):

\[
\langle \nu | \hat{H} | \Psi \rangle = \Delta E_{SD} \langle \nu | \Psi \rangle \quad \forall \ \nu \in \{ \Phi, \Phi_i^a, \Phi_{ij}^{ab} \} \quad (3)
\]
where we have used $\hat{P} = \hat{P}^2 = \hat{P}^\dagger$ and $[\hat{H}, \hat{P}] = 0$. This set of equations can be solved as a generalized eigenvalue problem,

$$\tilde{\mathbf{H}} \mathbf{c} = \Delta E_{\text{SD}} \mathbf{S} \mathbf{c}$$

(4)

where $\tilde{\mathbf{H}}$ and $\mathbf{S}$ are the Hamiltonian and overlap matrix elements in the basis of projected determinants.

As is widely known, it is not practical to employ Löwdin’s spin-projection operator even for a single broken-symmetry determinant, because the operator in this form is characterized as an intractable many-body manifold. Obviously, each excited determinant is further spin-contaminated compared to $|\Phi\rangle$, and therefore the use of this traditional operator would make ECISD completely infeasible. Instead, we use the integration scheme with one-body spin-rotation operator $\hat{R}(\Omega)$.

$$\hat{P} = \int_{\Omega} d\Omega \; w(\Omega) \hat{R}(\Omega) \simeq \sum_g w_g \hat{R}_g$$

(5)

where the numerical integration usually requires $7 \sim 10$ grid points. For more details, see Ref. [12].

Given Eqs. (4) and (5), our task is to formulate the matrix elements where ket is unitarily rotated with $\hat{R}_g$. Hence, it is convenient to introduce unitarily transformed fermions,

$$b_p^\dagger = \hat{R}_g a_p^\dagger \hat{R}_g^{-1} = \sum_q R_{pq} a_q^\dagger,$$

(6)

with $R_{pq} = \langle \phi_p | \hat{R}_g | \phi_q \rangle$. Note $\hat{R}_g |\Phi\rangle \equiv \prod_i b_i^\dagger |\rangle$ is a single Slater determinant nonorthogonal to $|\Phi\rangle$ with the physical vacuum $|\rangle$, and fermions $b_p$ depend on $g$. For our present purpose, we need to evaluate the transition density matrix element of an arbitrary string in the form,

$$\langle \Phi | a_{i_1}^\dagger \cdots a_{j_1}^\dagger a_{i_2} \cdots a_{j_2} \cdots a_{i_N}^\dagger \cdots a_{j_N} | \Phi \rangle$$

$$= \langle a_{i_1}^\dagger \cdots a_{i_N}^\dagger | a_{i_2} \cdots a_{i_N} \cdots a_{j_N} | \rangle \langle b_{j_1}^\dagger \cdots b_{j_N}^\dagger | b_{j_1} \cdots b_{j_N} | \rangle,$$

(7)

where we introduced the short hand notation,

$$\langle \cdots \rangle_g \equiv \frac{\langle \Phi | \cdots \hat{R}_g | \Phi \rangle}{\langle \Phi | \hat{R}_g | \Phi \rangle}.$$

The seminal works of Löwdin showed the way to calculate the transition density matrix of an arbitrary operator in terms of the one-body transition density matrix as a fundamental invariant. Nevertheless, the formulation based on the first quantization is not fully convenient to construct many-body theory including the spin projection operators. Inspired by Löwdin’s invariant, we develop the nonorthogonal Wick theorem to efficiently evaluate the transition density matrix elements in what follows.

Similarly to the extended Wick theorem for the MR case, a normal ordered operator for two nonorthogonal determinants can be expressed by subtracting the expectation values order-by-order in the operator rank. The fact that the expectation value for the nonorthogonal Slater-determinants is factorizable into one-body transition density matrices may allow us to express the normal ordered operator in exactly the same manner as the single-reference one in an orthogonal basis,

$$\langle \cdots \rangle_g + \sum_{\text{all contractions}} \{\cdots \}$$

(9)

in addition to the usual contractions for the fermions, $a_i^\dagger a_j^\dagger = b_i^\dagger b_j^\dagger = \delta_{ij}$. Here $o$ and $v$ indicate the occupied and virtual spaces of the molecular orbitals of $|\Phi\rangle$. $\mathcal{W}_g$ becomes the identity matrix in the case of regular single-reference methods, thus being unique to nonorthogonal methods. Then, the projected matrix elements can be solely expressed by $\mathcal{W}_g$ (along with $\delta$ functions for $\langle a_i^\dagger a_j \rangle_g$ and $\langle b_i^\dagger b_j \rangle_g$) using the nonorthogonal Wick theorem.

One of the major disadvantages of PHF methods, including SUHF, is that they are not size-consistent except for some special cases. Therefore, one of the most desirable features we expect for the residual correlation effect in post-PHF methods is size-consistency and, if possible, the capability of removing, or at least mitigating the size-consistency error resulting from PHF. However, since ECISD truncates the full-CI (FCI) expansion at doubles and neglects simultaneous double excitations, its correlation energy obviously does not have the proper scaling with respect to the system size. To correct this, we consider, in analogy with regular CISD and MRCI, an a posteriori treatment of approximate quadruple excitations using the Davidson correction scheme. Generally, a variety of the Davidson corrections require the CI coefficient $c_0$ of the reference wave function, e.g., the simplest one being $\Delta E_Q = (1 - c_0^2) \Delta E_{\text{SD}}$. In ECISD, on the other hand, this equation is not directly applicable because our reference wave function $\hat{P}|\Phi\rangle$ permeates the singles and doubles spaces through $\hat{P}$, as manifested by the fact $\langle \Phi | \hat{P} | \Phi \rangle \neq 0$. The role of $c_0^2$ in the Davidson corrections for (MR)CISD is that it carries the information about the weight that the reference state occupies in the space spanned by $|\Phi\rangle$. Hence, one can introduce operator
\[ \hat{O} = \hat{P}\Phi \langle \Phi | \hat{P} \Phi \rangle^{-1} \langle \Phi | \hat{P} \rangle, \] which performs projection onto the SUHF subspace. A “\(e^2\)–like” quantity can then be simply defined as the expectation value of \(\hat{O}\), and the Davidson correction becomes

\[ \Delta E_Q = \left( 1 - \frac{|\langle \Phi | \Psi \rangle|^2}{\langle \Phi | \hat{P} \Phi \rangle \langle \Psi | \Psi \rangle} \right) \Delta E_{SD}. \quad (11) \]

While there are several variants of a posteriori size-consistent corrections, we found that most schemes gave similar results for the molecules we have tested below, and hence we will only report the results with Eq. (11).

Before proceeding to the numerical results, we describe the computational details. In our implementation of ECISD, the diagonalization of Eq. (11) is carried out with direct CI employing the iterative technique due to Davidson extended to a generalized eigenvalue problem. ECISD with the simple diagonal preconditioning typically takes three-four times the number of cycles compared to regular CISD. We will address ways to ameliorate this slow convergence in a forthcoming paper. We use the converged SUHF orbitals within a variation-after-projection scheme, which are then fixed during the ECISD calculations. In the calculations of \(N_2\), 1s orbitals are frozen to enable the direct comparison against the exact FCI results. The active spaces used in CASPT2 and internally-contracted MRCI are (2e, 2o) for HF, (6e, 5o) for \(H_2O\), and (6e, 6o) for \(N_2\). We have used a 6-31G basis for all the calculations except for the \(H_{12}\) plane where a STO-3G basis was employed. Although regular CISD is obsolete, we also included it in our discussion to show the improvement ECISD has to offer.

We first demonstrate the performance of ECISD using the dissociation of the \(N_2\) molecule, which still largely remains challenging for major single reference methods such as CCSD. This system requires a considerable amount of dynamic correlation in the vicinity of equilibrium while the correct treatment of static correlation is indispensable as the internuclear distance increases. This is clearly seen in Figure 1; all the tested single-reference methods bring dynamic correlation and drastically improve the description over HF around equilibrium, but become inaccurate when the molecule is pulled apart. This deficiency is mostly attributed to the inadequacy of the HF reference. Energetically correct pictures for static correlation may be alternatively obtained by breaking the spin-symmetry of a wave function at the price that the result unrestricted wave function is not an eigenfunction of the spin operator. Therefore, while unrestricted HF (UHF) depicts the correct shape of the dissociation curve, many physical properties such as excitation energies are vastly incorrect. On the other hand, SUHF restores the spin-symmetry in the reference broken-symmetry HF determinant \(\Phi\) and describes the dissociation limit correctly; however, it significantly underestimates the correlation energy due to the lack of major dynamic correlation effects. ECISD delivers the residual correlation that is missing in SUHF, while retaining the correct description of static correlation. Noteworthy is that, not only at the dissociation limit where static correlation is abundant, but also at the equilibrium distance, ECISD outperforms CISD, and is as accurate as CCSD. We deem this is simply because even around this region SUHF provides a much better reference than does HF as a starting point.

Figure 2 illustrates the errors in mHartree from the FCI energy for the potential curves of HF, the symmetrically stretched \(H_2O\) at 109.57°, and \(N_2\). These three examples showcase the hierarchy of entanglements; two, four, and six electrons are strongly correlated, respectively, and an accurate description becomes harder to achieve in this order. For comparison, the results of unrestricted methods and CASPT2 are also plotted. Vertical dashed lines are added at experimental \(R_e\) as an eye guide, and the non-parallellity errors (NPE), the absolute difference between the maximum and minimum deviations from the FCI energy, are summarized in Table I. Again, ECISD achieves a significant improvement over UCISD at the same computational scaling and gains an accuracy comparable to UCISD(T). Its error, however, grows with the number of electrons \(N_e\) due to the size-consistency error as expected. The NPE also slightly increases with the number of entangled electrons as is evident from the results of isoelectronic systems, HF (NPE of 0.91 mH) and \(H_2O\) (3.77 mH), for the reason that will become clear shortly. Notice a similar deterioration can be observed in unrestricted methods, but for a different reason—spin-contamination. The spin-contamination error is largest halfway to dissociation, the region where static correlation can no longer be mimicked by simply breaking spin-symmetry. Consequently, the NPEs of size-consistent UCISD(T) are also appreciably large for all the tested systems. MR methods (CASPT2 and MRCI) are stable in this regard because they use CASSCF as the reference, and hence yield quantitatively accurate results but with a steep increase of the computational cost. UCISD suffers from both size-consistency error and spin-contamination error. Comparing the results for HF and \(H_2O\), we find the significance of the size-consistency error in UCISD (approximately quanti-
intriguing, given that $\Delta$ size-consistency error inherent to SUHF. This result is the error in ECISD almost disappears in spite of the $E$ not to $E$; it indicates that, while $\Delta E_{SD}$ itself is size-inconsistent, it yet mitigates the size-consistency error of SUHF. As a result, not only does ECISD+Q give remarkable small NPEs, but also it is almost exact in energy along the entire nuclear coordinates for all the test cases. It is also worth noting that in all the cases its accuracy can also depend on the number of entangled electrons, as is indeed the case.

When size-consistent correction $\Delta E_Q$ is introduced, the error in ECISD almost disappears in spite of the size-consistency error inherent to SUHF. This result is intriguing, given that $\Delta E_Q$ is a correction to $\Delta E_{SD}$ but not to $E_{SUHF}$; it indicates that, while $\Delta E_{SD}$ itself is size-inconsistent, it yet mitigates the size-consistency error of SUHF. As a result, not only does ECISD+Q give remarkably small NPEs, but also it is almost exact in energy along the entire nuclear coordinates for all the test cases. It is also worth noting that in all the cases its accuracy at equilibrium is of the CCSD(T) level of theory, which is the “gold-standard” with a $O(N^7)$ cost. Incidentally, MRCI+Q gives smaller NPEs than does ECISD+Q as expected, but at the cost of larger computational complexity.

Finally, we show an even more challenging system for strong correlation: the $4 \times 3$ hydrogen lattice. This system has been studied by other authors as a model system that represents a metal-insulator transition as the lattice parameter $a$ increases. When $a \to \infty$, its electronic structure exhibits very complicated spin-entanglement, and its complete description requires an active space of $(12e, 12o)$, which is nothing but FCI for a minimal STO-3G basis and requires 853,776 determinants. As shown in Figure 2, while many sophisticated spin-restricted and unrestricted methods break down for this system, both ECISD and ECISD+Q offer a balanced description between dynamic and static correlations. Their NPEs are found to be 8.01 and 2.84 mH, respectively. Our schemes accomplish this feat only with 1819 determinants, exactly the same number needed for single and double substitutions.

In summary, we proposed spin-extended CISD as a promising alternative to sophisticated traditional MR methods for strongly correlated systems. ECISD provides a black-box, cost-effective treatment of dynamic and static correlations in a balanced way. A remarkable accuracy was achieved when an approximate quadruples approximation is introduced through the adapted Davidson correction. However, ECISD+Q is an $a$ posteriori approach and thus works only for ground state energies, and further developments remain to be seen. We are currently working along this line.

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