

Orbital Energies for Seniority-Zero Wave Functions

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ABSTRACT: A new single-pair operator for seniority-zero wave functions is introduced closely related to the single-particle Fock operator from conventional Hartree–Fock theory. This allows one to ascribe orbital energies in the context of model Hamiltonians, for which no single-particle operators exist. Several applications demonstrate the usefulness of these orbital energies. In analogy to Koopmans’ theorem, atomic double ionization potentials are successfully predicted. A computationally efficient second-order perturbation scheme for seniority-zero wave functions scaling quadratically with system size is defined and applied to the dissociation of nitrogen and to strongly correlated two-dimensional Heisenberg lattices. An extension of the method for full seniority is presented leading to an intruder-free single reference perturbation theory with improved asymptotic convergence.

Pair orbital energies

occupied
 $\varepsilon_i = -\langle 0|a_i^\dagger \hat{H} a_i|0\rangle + \langle 0|\hat{H}|0\rangle$

virtual
 $\varepsilon_a = \langle 0|a_a \hat{H} a_a^\dagger|0\rangle - \langle 0|\hat{H}|0\rangle$

INTRODUCTION

Seniority, being a recently introduced concept into quantum chemistry, is a way of classifying wave functions by counting the maximum number of unpaired electrons in the Slater determinants of a configuration interaction (CI) expansion.^{1,2} Seniority-zero wave functions are the lowest rung on this ladder and employ only closed-shell determinants in a given orbital basis. Hence, they necessarily describe systems with an even number of electrons. The most general seniority-zero wave function comprises a fully flexible linear combination of all possible closed-shell Slater determinants leading to the factorially scaling doubly occupied CI (DOCI) method.³ Since DOCI is missing any energy contribution from open-shell determinants, care must be taken that properly rotated orbitals are used to capture a maximum of electron correlation.^{4–9} This can be achieved using a self-consistent field (SCF) procedure, ensuring a stationary energy with respect to a variation of the molecular orbital coefficients.^{10–12} Together with optimized orbitals, DOCI is an adequate tool to describe the effects of strong electron correlation, while a substantial fraction of dynamical correlation is not recovered by the method.¹³

An inexpensive and often sufficiently accurate way to account for dynamical correlation is the application of second-order perturbation theory (PT). There are many formulations of PT, especially for multi-reference wave functions.^{14–20} One fundamental decision that even leads to different branches of single reference (SR) PT is the partitioning of the full Hamiltonian \hat{H} into a zeroth-order Hamiltonian \hat{H}_0 and a fluctuation potential.²¹ The most famous partitioning schemes in SR PT are those of Möller–Plesset (MP) and Epstein–Nesbet (EN).^{22–24} The former employs the Fock operator for \hat{H}_0 , whereas the latter simply uses the diagonal elements of \hat{H} while setting all out-of-diagonal elements to zero. Although each \hat{H}_0 leads to a different zeroth-order energy, the MP and EN partitionings both possess the same energy at first order, namely, $E_0 + E_1 = \langle 0|\hat{H}|0\rangle$, corresponding to the energy of a normalized reference determinant $|0\rangle$. The first energy

improvement happens at second order and is given by the expression

$$E_2 = \sum_K \frac{\langle 0|\hat{H}|K\rangle \langle K|\hat{H}|0\rangle}{\langle 0|\hat{H}_0|0\rangle - \langle K|\hat{H}_0|K\rangle} \quad (1)$$

containing a sum over all doubly excited states $|K\rangle$. These states can be either Slater determinants or configuration state functions leading to different results in the case of an EN partitioning.²⁵ For wave functions with strong multi-reference character, MP and EN are plagued with intruder state problems, when certain energy denominators approach zero. Several methods have been developed to deal with this issue and to extend the applicability of PT also to strongly correlated systems.^{26–28} An alternative way based on replacing the Fock operator by seniority-zero matrix elements is presented in this study.

In seniority-zero wave functions, electrons will always be paired in the sense that whenever an orbital p is occupied, its twin orbital \bar{p} must be occupied as well, and vice versa. It should be noted that p and \bar{p} are not necessarily the α and β spin-orbitals of the same spatial extent (restricted DOCI) but can have different spatial shapes (unrestricted DOCI) and even contain spin-orbitals with mixed spin (generalized DOCI), without changing the concept of seniority at all.¹¹

When working with seniority-zero wave functions, the form of creation and annihilation operators in the formalism of second quantization is considerably simplified.²⁹ The operators a_p^\dagger and a_p for adding and removing individual electrons in orbital p must now always act pairwise as $S_p^\dagger = a_p^\dagger a_{\bar{p}}^\dagger$ and $S_p = a_{\bar{p}} a_p$. Together with the number operator

$$\hat{n}_p = a_p^\dagger a_p = a_{\bar{p}}^\dagger a_{\bar{p}} = \hat{n}_{\bar{p}} = S_p^\dagger S_p \quad (2)$$

these three operators define the entire algebra within the subspace of seniority-zero wave functions. A generic quantum chemical Hamiltonian of full seniority

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$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \sum_{pr} \sum_{q>p} \sum_{s>r} V_{pqrs} a_p^\dagger a_q^\dagger a_s a_r + H_{\text{nuc}} \quad (3)$$

with one- and antisymmetrized two-electron integrals h_{pq} and V_{pqrs} and constant nuclear repulsion H_{nuc} can be split into a seniority-zero part and a remainder $\hat{H} = \hat{H}_{\text{SZ}} + \hat{H}_{\text{R}}$, where \hat{H}_{R} always will evaluate to zero when bracketed by seniority-zero wave functions. The seniority-zero part can be written in a compact form as

$$\hat{H}_{\text{SZ}} = \sum_p d_p \hat{n}_p + \sum_{q>p} d_{pq} \hat{n}_p \hat{n}_q + \sum_{q \neq p} g_{pq} S_p^\dagger S_q + d_0 \quad (4)$$

with the summation running over the number of orbital pairs m . Table 1 shows how the coefficients of eqs 3 and 4 are

Table 1. Parametrization of d_p , d_{pq} , g_{pq} , and d_0 in eq 4 for Different Types of Hamiltonians

	RQC ^a	RG ^b	Heisenberg ^c
d_p	$2h_{pp} + J_{pp}$	ϵ_p	$\mu_p - \sum_{q \neq p} J_{pq}^z$
d_{pq}	$4J_{pq} - 2K_{pq}$	0	$2J_{pq}^z$
g_{pq}	K_{pq}	g_{pq}	J_{pq}^x
d_0	H_{nuc}	0	$-1/2 \sum_p (\mu_p - \sum_{q \neq p} J_{pq}^z)$

^aRestricted quantum chemical Hamiltonian with one-electron integrals h_{pq} , Coulomb and exchange integrals J_{pq} , K_{pq} , and nuclear repulsion H_{nuc} . ^bRichardson–Gaudin model with single-particle energies ϵ_p and individual pairing strength g_{pq} . ^cSpin-1/2 Heisenberg XXZ model, with axial coupling constants J_{pq}^z , equatorial coupling constants J_{pq}^x , and site energies μ_p induced by the external magnetic field.

interrelated for restricted orbitals. \hat{H}_{SZ} has only one off-diagonal term remaining, which corresponds to the excitation of an electron pair from orbital q to orbital p . Such Hamiltonians appear also in statistical mechanics or nuclear physics. The Richardson–Gaudin model for example assumes attractive or repulsive pairing forces between Fermions distributed in single-particle levels of different energies.^{30–33} Such a pairing Hamiltonian is a special case of the seniority-zero Hamiltonian from eq 4 as shown in Table 1. Furthermore, also the Heisenberg model for spin-1/2 systems belongs to the class of seniority-zero Hamiltonians.³⁴ With the aid of a Jordan–Wigner transformation, the meaning of S_p^\dagger and S_p is changed from pair creation and annihilation operators to ladder operators causing spin-flips on site p of a spin-1/2 cluster.³⁵ The different spin-states on each site interact energetically through (possibly anisotropic) coupling constants J_{pq} and also with an external magnetic field that can be modeled by eq 4 using the parametrization of Table 1. Since the Richardson–Gaudin model and the Heisenberg model are fully comprised by the seniority-zero Hamiltonian, both are exactly solvable with DOCI without any orbital rotation being necessary. For such model systems, full CI is identical to DOCI in the basis of localized sites.

Recent advances in geminal wave function theory made it possible to calculate the ground-state energy of many seniority-zero Hamiltonians to a very high accuracy at mean-field-like computational cost.³⁶ The energy differences between antisymmetrized products of one-reference-orbital geminals (AP1roG) and DOCI are typically in the order of only a few tenths of a milli-hartree, even for molecules with a large multi-reference character.¹³ So far, the only qualitative failure of AP1roG has been found for the attractive pairing model

Hamiltonian.^{37,38} The computational cost of AP1roG for pure seniority-zero wave functions is cubic. For quantum chemical Hamiltonians of full seniority, however, orbital optimization is a mandatory implication, which increases the computational cost. Exploiting the sparsity of two-electron integrals, the orbital transformation can be performed in quartic time. This is because at most three-index quantities are needed to calculate seniority-zero orbital gradients, which saves 1 order of magnitude in comparison to a full two-electron integral transformation. The overall scaling for AP1roG including orbital optimization is thus quartic. This low computational cost renders AP1roG a promising method to study strong electron correlation as appearing in bond-breaking, transition metal complexes, and strongly correlated matter in general.

Although branching from a more general family of geminal product wave functions, the AP1roG method is in fact identical to pair coupled cluster doubles (pCCD) theory, a simplified version of coupled cluster doubles, where only amplitudes corresponding to excitations within the seniority-zero subspace have weights different from zero.³⁹ The capabilities of AP1roG to accurately describe multi-reference systems, although being a simplification of a SR theory, recently inspired Scuseria and co-workers to develop approaches for adding dynamical correlation.^{40,41} Their frozen pair coupled cluster method starts with an ordinary AP1roG calculation using optimized orbitals, followed by a traditional coupled cluster calculation at any desired level of theory but with every pair amplitude fixed at its initial AP1roG value.

The somewhat surprising link of a geminal product method, intended to tackle strongly correlated problems, with a traditional method for dynamical correlation raises the question of further analogies between established quantum chemical concepts and quantities in the relatively new field of seniority-truncated wave functions, which will be addressed by the present article. Its content is structured as follows: In a first theoretical section, we will derive pair orbital energies, which are byproducts of a generic AP1roG calculation. It is then shown how closely they relate to conventional orbital energies defined as diagonal elements of the Fock matrix. After the Theory section, some illustrative applications are presented, where the Fock orbital energies have been replaced by pair orbital energies. These are namely (i) double ionization potentials and electron affinities in close analogy to Koopmans' theorem, (ii) a PT for seniority-zero wave functions in analogy to the conventional MP2 and EN2 methods, and (iii) derived thereof, a new intruder-free SR PT with two tunable parameters for wave functions of full seniority.

THEORY

Intermediates for a Fast Solution of the Projection Equations. The energy of an AP1roG is obtained by projecting the electronic Schrödinger equation onto a reference determinant $\langle 0|$ and pair excited determinants $\langle i\bar{i}^a| = \langle 0|S_i^\dagger S_{\bar{i}}^a$ yielding the expressions

$$E = \langle 0|\hat{H}|\psi\rangle \quad (5)$$

$$\Omega_{ia} = \langle i\bar{i}^a|\hat{H}|\psi\rangle - E\langle i\bar{i}^a|\psi\rangle \quad (6)$$

for the energy and residuals Ω_{ia} . $|\psi\rangle$ is intermediately normalized and defined as

$$|\psi\rangle = \prod_i^n (S_i^\dagger + \sum_a^k c_{ia} S_a^\dagger) |0\rangle \quad (7)$$

using the common notation i, j for the n occupied orbitals and a, b for the k virtual orbitals in the reference determinant $|0\rangle$. p, q refer to arbitrary elements of the $m = n + k$ orbitals. $|0\rangle$ denotes the vacuum state, which is the physical vacuum for quantum chemical Hamiltonians or the ferromagnetic vacuum in the case of Heisenberg lattices. Insertion of eqs 4, 5, and 7 into eq 6 yields a set of coupled nonlinear equations

$$\begin{aligned} \Omega_{ia} &= D_{ia} c_{ia} + g_{ai} - 2(A_{aa} + A_{ii}) c_{ia} + 2g_{ia} c_{ia}^2 + \sum_{j \neq i}^n g_{ji} c_{ja} \\ &+ \sum_{b \neq a}^k g_{ab} c_{ib} + \sum_j^n A_{ji} c_{ja} \stackrel{!}{=} 0 \end{aligned} \quad (8)$$

which can be solved for the geminal coefficients c_{ia} . Once these equations are converged and all coefficients are determined, they specify the AP1roG energy according to eq 5. In our implementation, Newton's method is applied to achieve convergence of eq 8. The computational cost of the algorithm is reduced to cubic scaling due to the introduction of intermediate quantities

$$A_{ba} = \sum_j^n g_{jb} c_{ja} \quad (9)$$

$$A_{ji} = \sum_b^k g_{jb} c_{ib} \quad (10)$$

Furthermore, all the diagonal elements of the Hamiltonian are collected in the term

$$D_{ia} = \langle a\bar{a} | \hat{H} | a\bar{a} \rangle - \langle 0 | \hat{H} | 0 \rangle = d_a - d_i + \sum_{j \neq i}^n d_{ja} - d_{ji} \quad (11)$$

such that all remaining terms in eq 8 contain only the coupling parameter g_{pq} of eq 4. The computational cost to evaluate the n -by- k matrix of eq 11 can be reduced to quadratic scaling when the intermediates

$$\varepsilon_i = \sum_j^n d_{ij} \quad (12)$$

$$\varepsilon_a = d_{aa} + \sum_j^n d_{aj} \quad (13)$$

are used, where the definitions $d_{pp} = d_p$ and $d_{qp} = d_{pq}$ are introduced. This simplifies eq 11 to

$$D_{ia} = \varepsilon_a - \varepsilon_i - d_{ia} \quad (14)$$

Pair Orbital Energies. It should be pointed out that the quantities ε have much in common with the diagonal elements of the Fock matrix, defined as

$$f_{pq} = h_{pq} + \sum_i^n V_{piqi} + V_{p\bar{i}q\bar{i}} \quad (15)$$

for a closed-shell reference determinant. The energy difference between $|0\rangle$ and a singly excited determinant $|i^a\rangle = a_a^\dagger a_i |0\rangle$ is expressed by means of the Fock matrix diagonal $f_p = f_{pp}$ as

$$\langle i^a | \hat{H} | i^a \rangle - \langle 0 | \hat{H} | 0 \rangle = f_a - f_i - V_{iaia} \quad (16)$$

which directly relates to eq 14. ε_p can thus be interpreted as an orbital energy, just like it is common practice for f_p , with the sole difference that ε_p accounts for the energy of a pair of electrons (p and \bar{p}) rather than a single electron. This is also mathematically reflected by the following equalities

$$\varepsilon_i = f_i + f_{\bar{i}} - V_{i\bar{i}i\bar{i}} \quad (17)$$

$$\varepsilon_a = f_a + f_{\bar{a}} + V_{a\bar{a}a\bar{a}} \quad (18)$$

that interrelate both kind of orbital energies to each other. For virtual orbitals, ε_a is simply the sum of the Fock energy of each individual orbital plus the pair repulsion energy for two electrons residing in orbital a . For occupied orbitals, the pair repulsion is subtracted, since the Fock elements account twice for it. Also the energy of the reference determinant can be written in terms of both kind of orbital energies as

$$\langle 0 | \hat{H} | 0 \rangle = \frac{1}{2} \sum_i^n h_i + f_i + h_{\bar{i}} + f_{\bar{i}} = \frac{1}{2} \sum_i^n d_i + \varepsilon_i \quad (19)$$

further emphasizing the close analogy between Fock orbital energies f_p and pair orbital energies ε_p . Note that above expressions stay valid for unrestricted and even generalized orbitals (where $f_p \neq f_{\bar{p}}$).

The decision whether f_p or ε_p should be used for orbital energies depends on the problem at hand. Performing a SR SCF procedure, certainly the Fock matrix is more adequate, as its off-diagonal values f_{pq} contain the necessary information for orbital optimization and allow to retrieve the symmetry-obedient canonical molecular orbitals. There is no meaningful definition of such off-diagonal elements for pair orbital energies, since these are derived from a seniority-zero Hamiltonian, which can only be formulated for a given set of orbitals (or sites in the case of model Hamiltonians). Hence, any arbitrary choice of orbitals to represent the full seniority Hamiltonian in eq 3 becomes automatically the natural orbitals in eq 4, which always possess a diagonal one-particle density matrix as well as diagonal orbital energies ε . When working with model Hamiltonians on the other hand, the absence of one- and two-electron integrals prohibits the specification of a Fock matrix. Then, orbital energies as defined by eqs 12 and 13 are the only possibility left.

In the following section, we present exemplary applications in which the Fock orbital energies f_p have been replaced by ε_p to illustrate the usefulness of pair orbital energies as a conceptual quantity and demonstrate its handiness to surmount difficulties arising from Fock orbital energies (or from the absence of them).

■ APPLICATIONS

Atomic Double Ionization Potentials. The most prominent example to give orbital energies a physical meaning is Koopmans' theorem, which directly relates occupied orbitals to ionization potentials and virtual orbitals to electron affinities.⁴² Adding or removing one electron in the reference determinant yields energy differences

$$\langle 0 | a_i^\dagger \hat{H} a_i | 0 \rangle - \langle 0 | \hat{H} | 0 \rangle = -f_i \quad (20)$$

$$\langle 0 | a_a \hat{H} a_a^\dagger | 0 \rangle - \langle 0 | \hat{H} | 0 \rangle = f_a \quad (21)$$

that correspond exactly to the definition of the Fock orbital energies. When two electrons are added or removed, the energy differences are given by

$$\langle 0|a_i^\dagger a_j^\dagger \hat{H} a_j a_i|0\rangle - \langle 0|\hat{H}|0\rangle = -f_i - f_j + V_{ijij} \quad (22)$$

$$\langle 0|a_b a_a \hat{H} a_a^\dagger a_b^\dagger|0\rangle - \langle 0|\hat{H}|0\rangle = f_a + f_b + V_{abab} \quad (23)$$

and, assuming $j = \bar{i}$ and $b = \bar{a}$, turn into

$$\langle 0|S_i^\dagger \hat{H} S_i|0\rangle - \langle 0|\hat{H}|0\rangle = -\varepsilon_i \quad (24)$$

$$\langle 0|S_a \hat{H} S_a^\dagger|0\rangle - \langle 0|\hat{H}|0\rangle = \varepsilon_a \quad (25)$$

using eqs 17 and 18. Since the orbital pairing scheme in the reference determinant is arbitrary, both formulations are equal. $-\varepsilon_i$ thus can be given a physical interpretation as double ionization potential (sum of first and second ionization potential) and ε_a as double electron affinity.

Tables 2 and 3 show calculated orbital energies in comparison with experimental ionization potentials. The

Table 2. Comparison of Experimental Ionization Potentials for Neutral Atoms Possessing a 1S_0 Electronic Ground-State with the Fock Energy of Canonical Orbital i Obtained from a HF/cc-pVQZ Calculation (in eV)

atom	term	i	exp. ^a	f_i	error ^b
He	$^2S_{1/2}$	$1s$	24.59	24.97	1.6
Be	$^2S_{1/2}$	$2s$	9.32	8.42	−9.7
Ne	$^2P_{3/2}$	$2p_z$	21.56	23.10	7.1
Mg	$^2S_{1/2}$	$3s$	7.65	6.88	−10.0
Ar	$^2P_{3/2}$	$3p_z$	15.76	16.08	2.0
Ca	$^2S_{1/2}$	$4s$	6.11	5.32	−13.0
Zn	$^2S_{1/2}$	$4s$	9.39	7.96	−15.3
Kr	$^2P_{3/2}$	$4p_z$	14.00	14.26	1.9

^aRef 48. ^bRelative error in percent.

Table 3. Comparison of Experimental Double Ionization Potentials for Neutral Atoms Possessing a 1S_0 Electronic Ground-State with the Pair Energy of Canonical Orbitals i and \bar{i} Obtained from a HF/cc-pVQZ Calculation (in eV)

atom	term	i	\bar{i}	exp. ^a	ε_i	error ^b
He	1S_0	$1s$	$1\bar{s}$	79.01	77.87	−1.4
Be	1S_0	$2s$	$2\bar{s}$	27.53	26.17	−4.9
Ne	3P_2	$2p_z$	$2p_y$	62.53	70.24	12.3
Mg	1S_0	$3s$	$3\bar{s}$	22.68	21.36	−5.8
Ar	3P_2	$3p_z$	$3p_y$	43.39	45.55	5.0
Ca	1S_0	$4s$	$4\bar{s}$	17.98	16.47	−8.4
Zn	1S_0	$4s$	$4\bar{s}$	27.36	24.44	−10.7
Kr	3P_2	$4p_z$	$4p_y$	38.36	39.85	3.9

^aRef 48. ^bRelative error in percent.

capability of pair orbital energies to predict double ionization potentials in Table 3 matches the predictive power of Koopmans' theorem illustrated in Table 2. In fact, the percental error is generally even lower. The exception are rare gases, where the doubly ionized ground state is a triplet and thus the picture of orbital pairing makes less sense. For atoms with a singlet double cation (in which both electrons are removed from the same spatial orbital), all errors significantly improve in comparison to Koopmans' theorem.

Since an estimation of electron affinities by Fock orbital energies is generally less accurate and atomic dianions are always unstable, we do not consider results for virtual orbital energies ε_a here.

Seniority-Zero Perturbation Theory. Another important occurrence of orbital energies is PT. Also here our goal is to obtain computational methods for seniority-zero wave functions analogue to MP2 and EN2 by replacing Fock orbital energies by pair orbital energies. These PT variants will be termed pMP2 and pEN2, in the same sense the name pCCD was coined for AP1roG. This will render it possible, for example, to perform SR PT calculations for Heisenberg lattices, as we illustrate below.

In an MP partitioning scheme, the zeroth-order Hamiltonian for seniority-zero wave functions is defined as

$$\hat{H}_0 = \sum_p \varepsilon_p S_p^\dagger S_p \quad (26)$$

leading to a second-order PT energy of

$$E_2^{\text{pMP}} = \sum_i^n \sum_a^k \frac{|\langle 0|\hat{H}|i\bar{i}^{a\bar{a}}\rangle|^2}{\varepsilon_i - \varepsilon_a} \quad (27)$$

For an EN partitioning, eq 1 turns into

$$E_2^{\text{pEN}} = \sum_i^n \sum_a^k \frac{|\langle 0|\hat{H}|i\bar{i}^{a\bar{a}}\rangle|^2}{\varepsilon_i - \varepsilon_a + d_{ia}} \quad (28)$$

straightforwardly derived from eqs 11 and 14. Because of the double-sum, E_2 is evaluated in quadratic computational time and thus can serve as a quick initial guess for a subsequent AP1roG calculation or as an estimate for the static correlation energy in its own right.

Figure 1 illustrates the improvement of pMP2 and pEN2 over their conventional versions for the dissociation of nitrogen. It is well known that SR PT methods completely fail to describe the breaking of this triple bond.⁴³ In Figure 1a, MP2 is seen to be at least accurate around the equilibrium structure, whereas EN2 cannot even locate a minimum and just monotonically decreases. In Figure 1b, only closed-shell determinants are considered and the conventional PT energy is replaced by the expressions above. The situation is now much improved with pEN2 being accurate around the equilibrium structure before diverging, whereas pMP2 maintains a qualitatively nearly correct description of the dissociation process, although significantly deviating from the proper DOCI solution.

The reason for this improvement is apparent from eqs 17 and 18. Even if all the Fock orbital energies are equal leading to a zero denominator in conventional MP2, the pair orbital energy levels stay separated by $V_{a\bar{a}a\bar{a}} + V_{i\bar{i}i\bar{i}}$ which is always larger than zero since both terms are repulsive Coulomb integrals. pEN2 diverges because of the additional term d_{ia} in the denominator. Of course the absolute energies obtained with seniority-zero methods are higher than those of full seniority approaches because of the missing dynamical correlation, but the differences between DOCI and full CI are close to a constant, about 0.25 hartree in Figure 1, as has been shown in a recent study.⁴⁴

Perturbation Theory for Lattices. Pair orbital energies have the benefit that they are available even in cases, where no Fock operator can be constructed, as for example in spin-

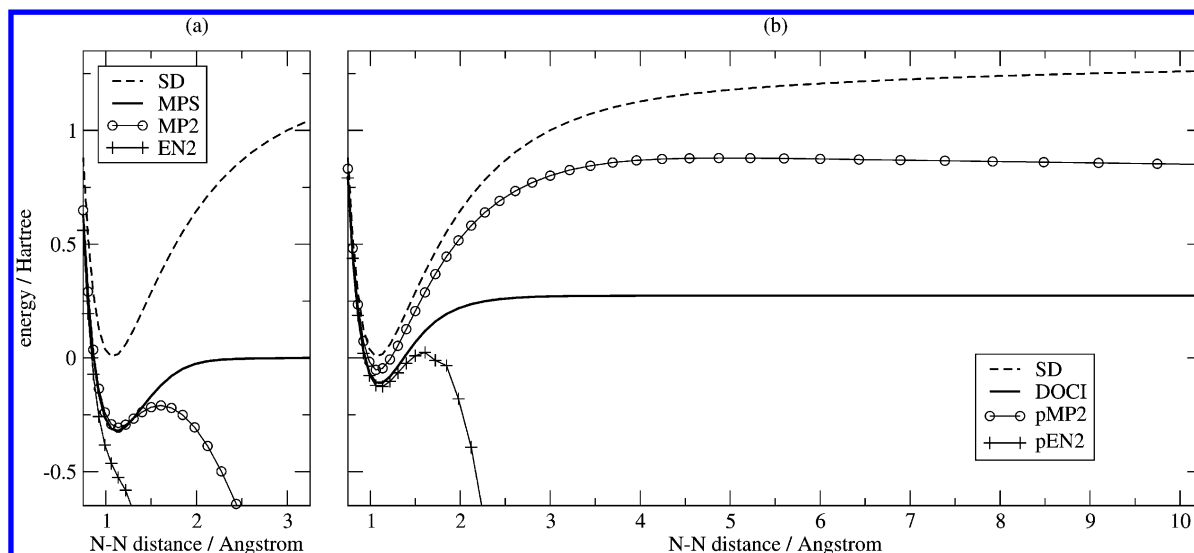


Figure 1. N_2 bond dissociation applying a cc-pVDZ basis set. Panel (a) shows full seniority PT methods (MP2 and EN2) in comparison to accurate matrix product state (MPS) calculations using a virtual dimension of $D = 2000$ in the CHEMPS2 program.^{50,51} Panel (b) shows the seniority-zero variants pMP2 and pEN2 in comparison to the DOCI solution. All calculations in both panels employ optimized DOCI orbitals. SD denotes the energy of a Slater determinant constructed from the seven most populated DOCI orbitals, which serves as the reference determinant in all PT calculations. SD was verified to closely follow the HF energy, in cases where SCF convergence could be achieved. All energies are presented relatively to the full CI energy of two infinitely separated atoms.

lattice models. Seniority-zero PT can be applied to spin-frustrated Heisenberg models simply by adhering to the Jordan–Wigner transformation rules provided in Table 1. Interestingly, SR methods such as seniority-zero PT and AP1roG are capable to describe some effects of strong electron correlation in these multi-reference problems.

Table 4 summarizes the PT results obtained for two kind of periodic two-dimensional Heisenberg lattices. A square lattice

Table 4. Pair Orbital Energies ϵ and Energy per Site (in units of J) of Various Methods Applied to Isotropic Antiferromagnetic Spin-1/2 Two-Dimensional Heisenberg Lattices with Periodic Boundary Conditions and Half-Filling ($S_z = 0$)

lattice	square	rhombic
ϵ_i	−2.0000 ^a	−1.0000 ^a
ϵ_a	2.0000 ^a	1.0000 ^a
E_{HF}	−0.5000 ^a	−0.2500 ^a
E_{pMP2}	−0.6250 ^a	−0.5000 ^a
E_{pEN2}	−0.6667 ^a	−0.7500 ^a
$E_{\text{AP1roG}}^{4 \times 4}$	−0.6573	−0.4562
$E_{\text{DOCI}}^{4 \times 4}$	−0.7018	−0.5347
$E_{\text{AP1roG}}^{\infty \times \infty}$	−0.6508	−0.4646
$E_{\text{DOCI}}^{\infty \times \infty}$	−0.6694 ^b	−0.5435 ^c

^aThese energies are independent of the lattice size. ^bRef 49. ^cRef 45.

with antiferromagnetic nearest-neighbor interactions and a triangular lattice with a rhombic unit cell, obtained from the square lattice by additional diagonal interactions between adjacent top-left and bottom-right sites.⁴⁵ Both systems possess a maximal multi-reference character in the sense that the exact DOCI wave function has no preferred spin orientation on each site (i.e., expectation values of $\langle \hat{n}_p \rangle = 1/2$ for all site populations). The seniority-zero PT methods are capable of recovering a fair amount of correlation energy without running into intruder state problems, since the orbital energies ϵ_i and ϵ_a

(which are the same for all sites due to translational invariance) stay well separated. Table 5 confirms the general observation

Table 5. Percental Correlation Energy Retrieved by pMP2, pEN2, and AP1roG for Square and Rhombic Heisenberg Lattices of Sizes 4×4 and Infinite

lattice	sq. 4	sq. ∞	rh. 4	rh. ∞
pMP2	66.9	73.8	87.8	85.2
pEN2	82.6	98.4	175.6	170.4
AP1roG	78.0	89.0	72.4	73.1

that pEN2 always recovers more correlation energy than pMP2 due to its smaller energy denominators, leading to a large overestimation in the case of the rhombic lattice. Consequently, pMP2 and AP1roG both return more reliable estimates than pEN2 in general. The excellent agreement between DOCI and AP1roG results, found for any quantum chemical Hamiltonian investigated hitherto, is lifted in this worst case scenario of highly frustrated spin-lattices. The same observation was made for the attractive pairing model.^{37,38} Nevertheless, AP1roG as a SR method recovers a respectable amount of $\sim 80\%$ from the total electron correlation. One should not forget that because of the inexpensive computational cost, it is easily possible to tackle lattices containing 1000 and more sites with this method.

Intruder-Free Perturbation Theory. It became clear in the last two sections why SR PT for seniority-zero wave functions can be applied to strongly correlated problems: The energy gap between frontier orbitals never reaches zero because the intrinsic Coulomb repulsion of each electron pair keeps them separated. This leads to nonvanishing energy denominators in eq 1.

In this section, we generalize the results to full seniority Hamiltonians by allowing, in addition to pair excitations $S_a^\dagger S_b$, also any other kind of double excitation $a_a^\dagger a_b^\dagger a_i a_j$. This can be achieved by defining the energy denominator in eq 1 by virtue of Koopmans' theorem as the sum of double ionization

potential and double electron affinity as derived in eqs 22 and 23. The result is an intruder-free SR PT with a second-order energy correction of

$$E_2 = \sum_{ij}^n \sum_{ab}^k \frac{|\langle 0 | \hat{H}_{ij}^{ab} \rangle|^2}{f_i + f_j - f_a - f_b - V_{ijij} - V_{abab}} \quad (29)$$

where the last two terms in the denominator guarantee a negative sign, even for completely degenerate Fock orbital energies $f_i = f_j = f_a = f_b$. Furthermore, the triangle inequality $|\langle 0 |$

$$E_2 = \sum_{ij}^n \sum_{ab}^k \frac{|\langle 0 | \hat{H}_{ij}^{ab} \rangle|^2}{f_i + f_j - f_a - f_b - \mu(V_{ijij} + V_{abab}) + \nu(V_{iaia} + V_{ibib} + V_{jaja} + V_{jbjb})} \quad (30)$$

with the introduction of two parameters μ and ν . Setting $\mu = 1$, $\nu = 0$, eq 29 is retrieved, whereas $\mu = \nu = 0$ corresponds to an MP and $\mu = \nu = 1$ to an EN partitioning scheme, respectively. Since μ and ν can be chosen arbitrarily, any intermediate partitioning is possible as well, ending up with a SR PT depending on few tunable parameters much in the spirit of spin-component-scaled MP2 and similar methods.^{46,47} The choice of μ and ν can be physically motivated. For example, an asymptotically correct dissociation of minimal basis H_2 requires $\mu = \nu + 1/2$ and converges fastest by choosing $\mu = 2$ and $\nu = 3/2$. This is in agreement with similar findings in the literature.²⁵

Figure 2 shows nitrogen dissociation curves for different choices of μ and ν . Being SR methods, all PT curves fail to

$\hat{H}_{ij}^{ab} \rangle| = |V_{ijab}| \leq V_{ijij} + V_{abab}$ ensures that the numerator will approach zero faster for decreasing V than the denominator. Hence, such a partitioning is completely free of intruder states, as long as the virtual Fock energies do not fall below the occupied Fock energies.

This intruder-free PT of full seniority is a hybrid between the two conventional MP and EN partitioning schemes in the literature, which becomes apparent when eq 29 is generalized to

qualitatively describe the accurate MPS calculation. Nevertheless, much improvement in the dissociation limit is gained in comparison to MP2 (with parameters $\mu = \nu = 0$). All methods with $\mu > \nu$ asymptotically approach a constant value, whereas MP2 keeps its linear decrease toward negative infinity. This finite PT energy at infinite bond separation may offer the possibility to improve the moderate second-order results in Figure 2 when higher-order perturbative corrections are included. It is expected that this new intruder-free PT will converge for cases, where the conventional MP2, MP3, MP4, etc. perturbative series diverges.

As a final remark, it should be pointed out that the intruder-free approaches proposed in this section generally recover less correlation energy around the equilibrium bond distance than conventional MP2 or EN2 due to larger energy denominators. This however does not allow to assess the accuracy of the method when relative energies, such as reaction or atomization energies, are of interest. Only a benchmark study on several test cases can answer this question and would allow to find optimal values for μ and ν in eq 30. Such data sets with particular emphasis on PT exist in the literature.^{46,47}

CONCLUSIONS

In the present study, seniority-zero wave functions are linked to established concepts of quantum chemistry for Hamiltonians of full seniority, and analogies are drawn between them. The core idea is to replace the one-particle Fock orbital energies by pair orbital energies directly available from coefficients in the seniority-zero Hamiltonian. This allows the definition of orbital energies in the framework of model Hamiltonians, where no Fock matrix can be employed. The pair orbital energies are straightforwardly derived from intermediates of an AP1roG calculation and have much in common with conventional Fock orbital energies. Most prominent is their physical interpretation as double ionization potentials and double electron affinities in analogy to Koopmans' theorem.

A reformulation of the second-order perturbation theory for pair orbital energies finds a seniority-zero PT scaling quadratically with system size. Although this approach, like the cubic AP1roG, depends on a reference determinant and thus by definition is a SR method, good estimates for the correlation energy of spin-frustrated Heisenberg lattices are obtained with both methods. For quantum chemical problems, orbital-optimization needs to be incorporated for accurate seniority-zero results and the computational cost grow with the fourth power of the system size. Using properly rotated orbitals, a qualitatively correct dissociation of the nitrogen triple bond

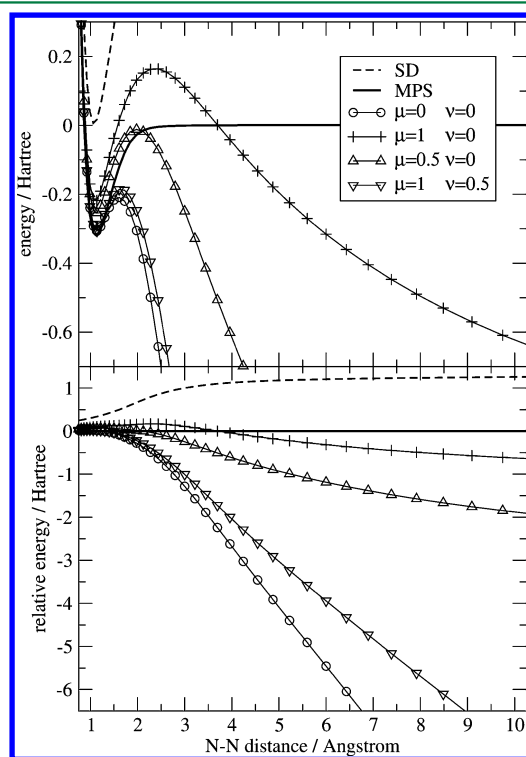


Figure 2. N_2 bond dissociation for different PT partitioning coefficients μ and ν according to eq 30 but adapted to a summation over configuration state functions instead of determinants. A cc-pVDZ basis set is applied. SD and MPS curves are the same as in Figure 1a. Energies are presented with respect to the full CI energy of two infinitely separated atoms (top) and as deviation from the MPS curve (bottom).

can be predicted with pMP2 in contrast to conventional full seniority MP2. This consolidates earlier findings that SR methods are capable to describe phenomena of strong electron correlation when treated at the seniority-zero level (i.e., with no open-shell determinants in a CI expansion). Furthermore, pMP2 can be utilized as a cheap and robust initial guess for the geminal coefficients of an AP1roG calculation.

When seniority-zero PT is generalized to full seniority, the resulting intruder-free PT retains some features to handle strongly correlated problems. Most noteworthy, the asymptotic convergence to a finite energy at complete bond dissociation contrasts the diverging energies from conventional MP or EN partitionings. The scope of treatable problems is thus enlarged and a convergent perturbative series might be obtained in cases, where conventional SR PT fails. Finally, multi-reference PT is expected to greatly benefit from the intruder-free replacement of the conventional Fock operator, abolishing one of its most cumbersome drawbacks.

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Notes

The authors declare no competing financial interest.

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