A New Mean-Field Method Suitable for Strongly Correlated Electrons: Computationally Facile Antisymmetric Products of Nonorthogonal Geminals

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We propose an approach to the electronic structure problem based on noninteracting electron pairs that has the similar computational cost to conventional methods based on noninteracting electrons. In stark contrast to other approaches, the wavefunction is an antisymmetric product of nonorthogonal geminals, but the geminals are structured so the projected Schrödinger equation can be solved very efficiently. We focus on an approach where, in each geminal, only one of the orbitals in a reference Slater determinant is occupied. The resulting method gives good results for atoms and small molecules. It also performs well for a prototypical example of strongly correlated electronic systems, the hydrogen atom chain.

I. The Electronic Structure Problem

Almost all of the commonly used qualitative and quantitative approaches to the electronic structure of molecules and materials are based on the orbital model. Electrons are assigned to the lowest-energy orbitals (also called single-particle states and one-electron wavefunctions), and coupled together only because each electron feels the average effect of the "cloud" of other electrons.[1] Mathematically, the wavefunction is an antisymmetric product of the occupied orbitals (i.e., a Slater determinant[2]) and the orbitals are obtained by solving a one-electron Schrödinger equation, where each orbital is coupled to the others only though an effective, possibly orbital-specific, one-body operator that depends on the other occupied orbitals.[1,3-6] Models of this type, including Hartree-Fock (HF) and Kohn-Sham density-functional theory, work well for many systems and, in particular, systems in which electrons move quasi-independently and in which the distinction between occupied and unoccupied "virtual" orbitals is unambiguous. In such cases, the residual errors can be mitigated by standard approaches including limited configuration interaction (taking a linear combinations of a few Slater determinants), coupled-cluster methods, and perturbation theories.[7-12]

The orbital model is *qualitatively* incorrect when distinguishing between occupied and unoccupied orbitals is unsuitable; such systems are said to be strongly correlated, and they are often said to have strong multireference character, because even a qualitatively correct description requires multiple (perhaps very many) Slater determinants.[13,14] Examples of strongly correlated electronic systems include molecules with stretched bonds, complexes of transition metals and/or Lanthanides, and superconductors. Developing efficient, robust, and easy-to-use methods for strongly correlated electronic systems is very important, but extremely difficult.

II. Wavefunctions Built from Electron Pair States, Geminals

The purpose of this paper is to present a new approach to electronic structure calculations, suitable for strongly-correlated electronic matter. Our model is based on a very old idea, an idea that even predates the concept of orbitals[15,16]: we consider the fundamental building block for the electronic wavefunction to be electron pair states.[17,18] (These electron pair states are described by two-electron wavefunctions that are typically called geminals or two-particle states.) The wavefunction we consider is an antisymmetric product of geminals (APG). In second-quantization,[7,19] the APG wavefunction has the form,[20,21]

$$\left|\Psi_{\text{APG}}\right\rangle = \prod_{p=1}^{P}\left(\sum_{k=1}^{2K}\sum_{l=1}^{2K} c_{p;kl} a_k^\dagger a_l^\dagger\right)\left|\theta\right\rangle \tag{1}$$

Here $\left|\theta\right\rangle$ denotes a suitable "vacuum" state and $a_k^\dagger$ is the operator that creates an electron in the k^{th} spin orbital. There are K spatial orbitals (and $2K$ spin orbitals) and there are $P = N/2$ electron pairs, where N is the number of electrons outside the vacuum reference state. (Whenever confusion is unlikely to arise, we will refer to spin-orbitals as simply "orbitals.") The vacuum state does not need to be a zero-electron state, but only the vacuum with respect to the creation of geminals. An odd number of electrons can therefore be treated by choosing a state with an odd number of electrons as the vacuum, but the alternative models we recently proposed could also be used.[22]

In Eq. (1), the factors in parentheses (p = 1, 2, …,P) are the geminals. By performing a change of basis, the complex expansion coefficients, $c_{p;kl} \in \mathbb{C}$, can be written in their equivalent “natural” form, in which the orbital-pairing scheme is explicit,[20,23]

$$\left|\Psi_{\mathrm{APG}}\right\rangle = \prod_{p=1}^{P}\left(\sum_{k=1}^{K} c_{p;k} a_{p;2k-1}^{\dagger} a_{p;2k}^{\dagger}\right)\left|\theta\right\rangle = \prod_{p=1}^{P}\left(\sum_{k=1}^{K} c_{p;k} a_{p;k}^{\dagger} a_{p;\bar{k}}^{\dagger}\right)\left|\theta\right\rangle \ . \tag{2}$$

In general, every geminal has a different characteristic orbital pairing scheme. By **C** we denote the $P \times K$ matrix containing the coefficients $c_{p;k}$.

The idea of constructing wavefunctions consistent with the Lewis structure of a molecule is very old, but it was quickly realized that the general APG form is computationally intractable.[21,24] Approximation techniques were quickly advanced, most of them based on the assumption of separated electron pairs.[20,25,26] With this assumption, the wavefunction takes the computationally tractable form of an antisymmetric product of strongly-orthogonal geminals (APSG).[17,18,21,27-32] In APSG, each orbital pair contributes to at most one geminal;[33,34] this severe assumption means that correlations between certain orbital pairs is omitted. Correlation between all possible orbital pairs is restored in the antisymmetric product of interacting geminals (APIG),[35,36]

$$\left|\Psi_{\mathrm{APIG}}\right\rangle = \prod_{p=1}^{P}\left(\sum_{k=1}^{K} c_{p;k} a_{k}^{\dagger} a_{\bar{k}}^{\dagger}\right)\left|\theta\right\rangle \tag{3}$$

but this form is also computationally intractable.[37] Notice that, unlike the general APG wavefunction (2), in the APIG wavefunction, the orbital-pairing scheme is restricted to be the same in all the geminals. Although it is often natural to restrict the orbital pairing scheme to "intuitive" patterns (e.g., choosing to pair orbitals that have the same spatial part, and differ only in spin), all the results in this paper hold for arbitrary "broken symmetry" geminals.[22,38,39]

The contribution of this paper is to present extremely accurate, yet computationally facile, approximations to the APIG wavefunction. To this end, we first write the APIG wavefunction as a sum over all Slater determinants with P occupied orbital pairs,[22]

$$\left|\Psi_{\text{APIG}}\right\rangle = \sum_{\left\{m_i=\{0,1\}\left|\sum_{k=1}^{K} m_k = P\right.\right\}} \left|\mathbf{C}(\mathbf{m})\right|^{+} \left(a_1^\dagger a_{\bar{1}}^\dagger\right)^{m_1}\left(a_2^\dagger a_{\bar{2}}^\dagger\right)^{m_2}\cdots\left(a_K^\dagger a_{\bar{K}}^\dagger\right)^{m_K}\left|\theta\right\rangle \tag{4}$$

where $\mathbf{C}(\mathbf{m})$ is the $P \times P$ matrix containing only the columns of $\mathbf{C}$ for which $m_k = 1$, and $\left|\mathbf{C}(\mathbf{m})\right|^{+}$ denotes the permanent of this matrix. The APIG wavefunction is a special case of the doubly-occupied (or pair-occupied, or seniority-zero) configuration interaction wavefunction (DOCI),[40-44] in which every orbital pair is either unoccupied or occupied by two electrons

$$\left|\Psi_{\text{DOCI}}\right\rangle = \sum_{\left\{m_i=\{0,1\}\left|\sum_{k=1}^{K} m_k = P\right.\right\}} c_{m_1 m_2 \ldots m_K} \left(a_1^\dagger a_{\bar{1}}^\dagger\right)^{m_1}\left(a_2^\dagger a_{\bar{2}}^\dagger\right)^{m_2}\cdots\left(a_K^\dagger a_{\bar{K}}^\dagger\right)^{m_K}\left|\theta\right\rangle \tag{5}$$

This wavefunction form, its simplifications, and its multi-configurational self-consistent field variants (in which the orbitals, and not just the coefficients, in Eq. (5) are optimized[43,45-51]) is widely considered to be an excellent model for the qualitative features of strongly correlated systems. (That is, DOCI recovers most of the "static correlation" in strongly correlated systems).[43,52-56] However, DOCI is not computationally tractable because the number of Slater determinants, $\binom{K}{P}$, grows exponentially with increasing system size.

III. Practical Approximations for the Antisymmetrized Product of Interacting Geminals (APIG)

APIG is difficult because (a) the Slater determinant expansion (4) includes a factorial number of determinants and (b) evaluating the permanent of a matrix is #P-hard (which implies that it is also NP-hard)[57]. The first problem is avoided by considering the projected Schrödinger equation,

$$\left\langle \Phi_{\text{test}} \middle| \hat{H} \middle| \Psi \right\rangle = E \left\langle \Phi_{\text{test}} \middle| \Psi \right\rangle \tag{6}$$

where Φ_{test} is an arbitrary wavefunction, but is usually chosen to be a Slater determinant of low energy. Because of the pair-excitation structure in APIG, the most interesting Slater determinants are obtained as pair excitations of a fully-paired reference Slater determinant,

$$\left| \Phi_{i\bar{i}}^{a\bar{a}} \right\rangle = a_a^\dagger a_{\bar{a}}^\dagger a_{\bar{i}} a_i \left| \Phi_0 \right\rangle \ . \tag{7}$$

The singly-excited determinants,

$$\begin{aligned} \left| \Phi_i^a \right\rangle &= a_a^\dagger a_i \left| \Phi_0 \right\rangle & \qquad \left| \Phi_i^{\bar{a}} \right\rangle &= a_{\bar{a}}^\dagger a_i \left| \Phi_0 \right\rangle \\ \left| \Phi_{\bar{i}}^{\bar{a}} \right\rangle &= a_{\bar{a}}^\dagger a_{\bar{i}} \left| \Phi_0 \right\rangle & \qquad \left| \Phi_{\bar{i}}^{a} \right\rangle &= a_a^\dagger a_{\bar{i}} \left| \Phi_0 \right\rangle \end{aligned} \tag{8}$$

and arbitrary (not-necessarily pair-excited) doubly-excited determinants are also potentially useful test vectors. Because the Hamiltonian is a 2-body operator,[7]

$$\hat{H}\left|\Psi\right\rangle = \left(\sum_{i,j=1}^{2K} h_{ij} a_i^\dagger a_j + \frac{1}{2}\sum_{i,j,k,l=1}^{2K} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k\right)\left|\Psi\right\rangle , \tag{9}$$

the projected Schrödinger equation only couples together Slater determinants that differ by one or two orbitals. If one chooses test determinants that are low-order excitations of the reference determinant, Φ_0, then most of the Slater determinants in the expansion (4) no longer contribute. For example, one could determine the *KP* unknown coefficients $c_{p;k}$ in the APIG wavefunction by minimizing the residual error in the (overdetermined) system of nonlinear equations obtained by considering all single-excited and pair-excited test determinants. The choice of reference determinant influences the projection space and therefore the final energy. We always choose the determinant with the lowest energy, i.e., the Hartree-Fock wavefunction.

The idea of using the projected Schrödinger equation with pair-excited determinants in antisymmetrized product of geminal wavefunctions originates with Cullen[58] and has been popularized by the Head-Gordon group[32,59,60]. Using intermediate normalization for the reference determinant, $\left\langle \Phi_0 \middle| \Psi_{\text{APIG}} \right\rangle = 1$, and considering, for simplicity, only the pair-excited determinants as the test wavefunctions, the projected Schrödinger equations for APIG are

$$\begin{aligned} E &= \left\langle \Phi_0 \middle| \hat{H} \middle| \Psi_{\text{APIG}} \right\rangle \\ 0 &= \left\langle \Phi_{i\bar{i}}^{a\bar{a}} \middle| \hat{H} \middle| \Psi_{\text{APIG}} \right\rangle - E\left\langle \Phi_{i\bar{i}}^{a\bar{a}} \middle| \Psi_{\text{APIG}} \right\rangle, \end{aligned} \tag{10}$$

which gives a system of nonlinear equations, one for each test determinant, $\Phi_{i\bar{i}}^{a\bar{a}}$,

$$
\begin{aligned}
0 = {} & \left(\left(h_{aa} - h_{ii} \right) + \left(K'_{aa} - K'_{ii} \right) + \sum_{\substack{j=1 \\ j \neq i}}^{P} \left(\left(J_{ja} - J_{ij} \right) - \left(K_{ja} - K_{ij} \right) \right) \right) p_i^a \\
& + K'_{ia} \left(1 - \left(p_i^a \right)^2 \right) + \sum_{\substack{b=P+1 \\ b \neq a}}^{K} \left(K'_{ab} - K'_{ib} p_i^a \right) p_i^b + \sum_{\substack{j=1 \\ j \neq i}}^{P} \left(K'_{ij} - K'_{ja} p_i^a \right) p_j^a \\
& + \sum_{\substack{j=1 \\ j \neq i}}^{P} \sum_{\substack{b=P+1 \\ b \neq a}}^{K} K'_{jb} \left(p_{ij}^{ab} - p_i^a p_j^b \right)
\end{aligned}
\tag{11}
$$

where

$$h_{mm} = h_{mm} + h_{\bar{m}\bar{m}} \tag{12}$$

$$J_{mn} = V_{mnmn} + V_{m\bar{n}m\bar{n}} + V_{\bar{m}n\bar{m}n} + V_{\bar{m}\bar{n}\bar{m}\bar{n}} \tag{13}$$

$$K_{mn} = V_{mnnm} + V_{\bar{m}\bar{n}\bar{n}\bar{m}} + V_{m\bar{n}\bar{n}m} + V_{\bar{m}nn\bar{m}} \tag{14}$$

$$K'_{mn} = V_{m\bar{m}n\bar{n}} - V_{m\bar{m}\bar{n}n} \tag{15}$$

(If one uses *non*-broken-symmetry geminals, where the orbitals that contribute to each orbital pair have identical spatial parts and differ only in spin, then the one-electron integrals, h_{mm}, Coulomb integrals, J_{mn}, and exchange integrals, K_{mn}, are defined in the conventional way.[7]) The notation $p_{ijk\cdots}^{abc\cdots}$ denotes the permanent of the $P \times P$ matrix in which the $i\bar{i}$, $j\bar{j}$, $k\bar{k}$,… orbital pairs (occupied in the reference state) are replaced by the $a\bar{a}$, $b\bar{b}$, $c\bar{c}$, … orbital pairs (occupied in the pair-excited state). Explicitly,

$$
\begin{aligned}
p_{ijk\cdots}^{abc\cdots} &= \left| \mathbf{C}\left(\mathbf{m} \right) \right|^{+} \\
m_n &= \begin{cases} 1 & 1 \leq n \leq P;\ n \neq i,j,k\ldots;\ n = a,b,c\ldots \\ 0 & P+1 \leq n \leq K;\ n \neq a,b,c\ldots;n = i,j,k\ldots \end{cases}
\end{aligned}
\tag{16}
$$

where $\left|\mathbf{C}(\mathbf{m})\right|^{+}$ is the permanent of the sub-matrix of **C** that contains column n only if $m_n = 1$. Eq. (11) is reminiscent of equations in refs. [37] and [58].)

The problem of evaluating the permanent is mitigated by structuring the coefficients of the geminals so that the permanents in Eq. (11) are easy to evaluate. Among the possible choices are:

- One-reference-orbital geminals; AP1roG. Choose the coefficients $c_{p;k}$ so that each geminal contains a contribution from one distinct orbital pair from the reference determinant; allow the coefficients corresponding to orbitals that are unoccupied in the reference determinant to be chosen arbitrarily. I.e., up to an arbitrary normalization factor, the coefficient matrix has the form,

  $$\mathbf{C}_{\text{AP1roG}} = \begin{bmatrix} 1 & 0 & \cdots & 0 & c_{1;P+1} & c_{1;P+2} & \cdots & c_{1;K} \\ 0 & 1 & \cdots & 0 & c_{2;P+1} & c_{2;P+2} & \cdots & c_{2;K} \\ \vdots & & \ddots & & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 & c_{P,P+1} & c_{P,P+2} & \cdots & c_{P,K} \end{bmatrix} \tag{17}$$

  With this choice, the permanents that enter Eq. (11) are easily evaluated,

  $$p_i^a = c_{i;a} \tag{18}$$

  $$p_{ij}^{ab} = c_{i;a}c_{j;b} + c_{i;b}c_{j;a} \tag{19}$$

  We call this wavefunction AP1roG because it is an antisymmetric product of geminals with one distinct "reference orbital" occupied in each geminal. For an appropriate choice of Φ_0, this form is a generalization of the APSG and generalized valence bond perfect pairing (GVB-PP) wavefunctions.[20,26,31,61,62] Like those wavefunction forms, AP1roG can be can be expressed as a type of coupled-cluster theory. Specifically, AP1roG is pair-coupled-cluster: CCD where only pair-excitations are allowed. I.e.,

$$\begin{aligned} \left|\Psi_{\text{AP1roG}}\right\rangle &= \prod_{i=1}^{P}\left(a_i^\dagger a_{\bar{i}}^\dagger + \sum_{a=P+1}^{K} t_i^a a_a^\dagger a_{\bar{a}}^\dagger\right)\left|\theta\right\rangle \\ &= \prod_{i=1}^{P}\prod_{a=P+1}^{K}\left(1+t_i^a a_a^\dagger a_{\bar{a}}^\dagger a_{\bar{i}} a_i\right)\left|\Phi_0\right\rangle \\ &= \exp\left(\sum_{i=1}^{P}\sum_{a=P+1}^{K} t_i^a a_a^\dagger a_{\bar{a}}^\dagger a_{\bar{i}} a_i\right)\left|\Phi_0\right\rangle \end{aligned} \tag{20}$$

AP1roG can be generalized to the case where each geminal contains contributions from at most *J* of the orbitals that are occupied in the reference state, where *J* is a small number. We call that wavefunction AP*J*roG. For *J* > 1, AP*J*roG, just like all of the other geminal forms we will propose, cannot easily be written as a variant of coupled-cluster theory.

- Element-wise inverse rank-two geminals, APr2G.[22] If the element-wise (i.e., Hadamard) inverse of the matrix **C** is a matrix of rank two, then the permanent can be written as a ratio of determinants,[63,64]

$$\left|\mathbf{C}(\mathbf{m})\right|^{+} = \frac{\left|\mathbf{C}(\mathbf{m})\circ\mathbf{C}(\mathbf{m})\right|}{\left|\mathbf{C}(\mathbf{m})\right|} \tag{21}$$

where ○ denotes the Hadamard product. So we choose the coefficients to have the form,[22]

$$c_{p;k} = \frac{\zeta_k}{\varepsilon_k - \lambda_p}. \tag{22}$$

This geminal form is inspired by the Bethe ansatz solution to a factorizable interaction, such as hyperbolic Richardson-Gaudin Hamiltonians. (I.e., the eigenvectors of the Richardson-Gaudin Hamiltonian have this functional form.[65-74] This is analogous to the relationship between an arbitrary Slater determinant and the actual solution to a system of Hartree-Fock equations.) We call this wavefunction APr2G. If the element-wise inverse matrix is of rank 1 (i.e., all the λ_p's are the same), then one has the antisymmetrized (broken-symmetry) geminal power wavefunction, APr1G.[38,39,75-80]

- Combination of APr2G and AP1roG. The reference-orbital portion of **C** can be chosen as in APr2G, and the rest of **C** can be chosen arbitrarily (as in AP1roG),

$$\mathbf{C}_{\text{APr2roG}} = \begin{bmatrix} \frac{\zeta_1}{\varepsilon_1 - \lambda_1} & \frac{\zeta_2}{\varepsilon_2 - \lambda_1} & \cdots & \frac{\zeta_P}{\varepsilon_P - \lambda_1} & c_{1;P+1} & c_{1;P+2} & \cdots & c_{1;K} \\ \frac{\zeta_1}{\varepsilon_1 - \lambda_2} & \frac{\zeta_2}{\varepsilon_2 - \lambda_2} & \cdots & \frac{\zeta_P}{\varepsilon_P - \lambda_2} & c_{2;P+1} & c_{2;P+2} & \cdots & c_{2;K} \\ \vdots & & \ddots & & \vdots & \vdots & \ddots & \vdots \\ \frac{\zeta_1}{\varepsilon_1 - \lambda_P} & \frac{\zeta_2}{\varepsilon_2 - \lambda_P} & \cdots & \frac{\zeta_P}{\varepsilon_P - \lambda_P} & c_{P,P+1} & c_{P,P+2} & \cdots & c_{P,K} \end{bmatrix} \tag{23}$$

We call this wavefunction APr2roG. Hybrids of the AP*J*roG and APr2G wavefunctions are also feasible.

All of these approximations are antisymmetric products of *nonorthogonal* geminals. While there are several practical computational methods using strongly orthogonal geminals, this is the first time, to our knowledge, that computationally practical wavefunctions based on nonorthogonal geminals have been presented.

The APIG wavefunction includes many others as special cases, including (a) APSG (the geminals are built from disjoint orbital sets; if $c_{p;k} \neq 0$ is nonzero, then $c_{q;k} = 0$ for all $q \neq p$), (b) The generalized valence bond-perfect pairing Hamiltonian (GVB-PP) (APSG, with the additional assumption that at most two orbital pairs contribute to a given geminal); (c) the antisymmetrized geminal power (AGP) (all the geminals are the same: $c_{k;p}$ is the same for all p),

(d) the eigenstates of Richardson-Gaudin Hamiltonians, and (e) most (if not all) cases of the projected Hartree-Fock-Bogoliubov electronic wavefunction.[38,81-83] Our new geminal approximations also include most of these as special cases.

Figure 1 exposes the mathematical framework that unifies these geminal-based methods: each method chooses a characteristic structure for the coefficient matrix, **C**, that facilitates numerical evaluation of the permanents in Eq. (11). **C** is arbitrary in APIG (which is why APIG is computationally intractable). Choosing **C** to be the Hadamard inverse of a low-rank matrix (APr*J*G, AGP) or to be (nearly) diagonal for the orbitals occupied in the reference determinant (AP*J*roG, APSG, GVB-PP) gives computationally tractable methods.

IV. Computations with AP1roG

We now show that even the simplest and most computationally efficient of these approximations, AP1roG using pair-excited Slater determinant test wavefunctions, gives results that are almost indistinguishable from DOCI.

Substituting Eqs. (18) and (19) into Eq. (11) gives a system of $P(K-P)$ quadratic equations to solve for the $P(K-P)$ unknown geminal coefficients, $c_{i;a}$; we solved these equations using a quasi-Newton method. Evaluating each equation costs $P(K-P)$ operations, with the only non-linear scaling term being the last one in Eq. (11). The overall scaling of determining AP1roG with pair-excited test wavefunctions is $O(P^2(K-P)^2)$. We used a naïve Slater determinant initial guess with $c_{p;a} = 0$. For the strongly correlated H_8 chain, the more natural GVB-PP initial guess ($c_{p;a} = -\delta_{p,a-p}$) was chosen. We did not consider broken-symmetry geminals: ϕ_m and $\phi_{\bar{m}}$ differ only in spin.

To test the accuracy of this method, we calculated the energy of several two-, four-, and ten-electron systems (Table 1). Except for the 10-electron Hydrogen molecule chains, the correlation energies of AP1roG and DOCI agree to within $\pm 10^{-5}$ a.u. (2×10^{-4} eV). (Because our approach is not variational, the AP1roG energy can be below the DOCI energy.) For $(H_2)_5$, the error is still small (no greater than 7×10^{-5} a.u; 2×10^{-3} eV), even though these systems are more strongly correlated than the other systems in Table I. As AP1roG is almost indistinguishable from DOCI and AP1roG is a special case of APIG, APIG must be an excellent approximation to DOCI.

All geminal methods, like DOCI, will be exact for 2-electron systems if the orbital basis set is optimized; this is reflected in Table 1. We have not optimized the orbitals separately for each method: in all cases the "exact" optimized orbitals are obtained from an orbital-optimized DOCI calculation, then these optimized orbitals are used in AP1roG, APSG, etc.. Optimizing the orbitals is helpful even for atoms, but it is especially important in separated molecules (He_2 and H_2 chains), where orbital optimization (partially) localizes the canonical Hartree-Fock orbitals, enabling the correct dissociation limits to be regained. With fully optimized orbitals, AP1roG is size-consistent; this is clear from the excellent results that are obtained for systems composed of well-separated 2-electron fragments, the near-exact results that are obtained for the stretched Helium dimer, and the link between AP1roG and coupled cluster (cf. Eq. (20)).

In systems like the Neon atom, where electron correlation is predominantly (perhaps entirely) dynamical, neither AP1roG nor DOCI recovers even half of the total correlation energy. However, in strongly correlated systems like chains of hydrogen molecules, where conventional electronic structure methods perform poorly, AP1roG (like DOCI) performs well. Recovering the residual dynamical correlation is usually relatively straightforward. For example, one can adapt the same methods that are used in conventional APSG[54-56] or use AP1roG to guide a quantum Monte Carlo calculation.[39,80,84]

The electronic structure of the systems in Table 1 is reasonably well described by the orbital model; the distinction between occupied and unoccupied orbitals is relatively unambiguous. A prototypical example of strong correlation is a chain of equally-spaced hydrogen atoms. Figure 2 shows the energy profile for stretching a linear chain of 8 equidistant hydrogen atoms, H_8. AP1roG is hardly distinguishable from DOCI over the entire range of interatomic distances, and is especially accurate in the strongly correlated $R \to \infty$ regime. The greatest deviation of our method from DOCI occurs for interatomic distances about 4 a.u., which is the region where the transition from linked "metallic" hydrogen atoms (with delocalized electronic states) to isolated hydrogen atoms occurs.[85] Even here, AP1roG differs from DOCI by less than 6×10^{-4} a.u. (2×10^{-2} eV). This is the same region where conventional Slater determinant + correction approaches like MP2 (second order Moller-Plesset perturbation theory) and CCSD (coupled cluster with single and double excitations) catastrophically fail.

Since AP1roG is a type of coupled-cluster method, we investigated whether the accuracy of traditional coupled-cluster approaches would be improved by using the same orbitals we use for AP1roG (i.e., orbitals optimized for DOCI). As shown in Figure 3a, CCSD and CCD with DOCI-optimized orbitals is more accurate than CCSD with canonical Hartree-Fock orbitals, but all three methods catastrophically underestimate the energy around 4 a.u., where the chemical bonds break. In addition, all the coupled-cluster methods converge slowly and erratically, and fail to converge entirely beyond a certain interatomic distance. CCSD and CCD with DOCI-optimized orbitals were particular problematic, failing to converge within 100,000 iterations at certain points in the bond-breaking regime (ca. 4 a.u.) and earlier in the dissociation regime than conventional CCSD. AP1roG converges nicely at all distances we considered. Its error is nearly a constant (which we attribute to dynamical correlation) for short interatomic distances and its error decreases smoothly towards zero as the interatomic separation increases.

Alternatively, AP1roG can be viewed as a geminal method, so we investigated how it performs compared to traditional geminal methods, specifically APSG and GVB-PP. These three methods are nearly indistinguishable on the energy scale of Figure 3a, so in Figure 3b we plot the errors in these geminal methods relative to DOCI, which is the most appropriate benchmark for any geminal method in the APIG family. AP1roG is the only geminal method that is correct at short interatomic distances, and never deviates by more than 6×10^{-4} a.u. from DOCI. In the dissociation limit, most of the geminal coefficients, $c_{p,k}$, are zero, and GVB-PP and APSG are both exact. As the interatomic separation decreases, first GVB-PP (about 5 a.u.) and then APSG (about 3 a.u.) break away from the DOCI potential energy curve. These methods struggle to describe the delocalized electronic states that typify the chemical bonding regime; they fail at short interatomic separations, with errors (relative to DOCI) of several milliHartree. For the most stable interatomic distances (about 2 a.u.), the AP1roG energy is almost exactly equal to the DOCI energy, but APSG and GVB-PP differ from DOCI by more than 1×10^{-3} a.u..

As mentioned previously and demonstrated in Table 1, DOCI and related methods are strongly orbital dependent. Figure 3 shows how the energies of DOCI and AP1roG change as the orbitals of methane are gradually transformed from the canonical Hartree-Fock orbitals, through the optimized DOCI orbitals, to the natural orbitals. While the canonical Hartree-Fock orbitals and the natural orbitals have the tetrahedral symmetry of CH_4, the optimal DOCI orbitals are the sp^3 hybrid orbitals. During the rotation from canonical orbitals to optimized DOCI orbitals, the AP1roG and DOCI energies are almost indistinguishable. As the DOCI orbitals are transformed into the natural orbitals, the DOCI energy increases dramatically, while the AP1roG energy increases by a much smaller amount. It is clear that AP1roG and DOCI do not always strongly resemble each other; it is necessary for optimized orbitals to be used in both methods. AP1roG seems less sensitive to orbital rotations than DOCI.

We observed that the last term in Eq. (11) was small in all our calculations. Neglecting this term gives a method with cubic scaling (excepting the transformation of the two-electron orbitals to the optimized orbital basis, which still scales as $O(K^5)$). The cubic-scaling method gives results that are almost indistinguishable from, albeit slightly less accurate than, the quartic scaling approach featured here.

V. Summary

The most challenging problem in modern electronic structure theory is the problem of strong correlation: how can one model the electronic structure of a system when the orbital picture breaks down? The idea of using electron pair wavefunctions, called geminals, to *explicitly* describe the pairing of electrons in strongly correlated systems is not a new one, but the forms that have been previously proposed are either chemically inappropriate (e.g., not size consistent[38,78]), require strong assumptions about the correlation between pairs of orbitals (e.g., strong orthogonality[20,26]), or are extremely computationally expensive[21,24]. The methods proposed here avoid all these problems. They are size-consistent and the optimized orbitals resemble the localized orbitals we expect from valence-bond theory. They are computationally facile even though the wavefunction ansätze are antisymmetrized products of nonorthogonal geminals with a rather general forms.

In the simplest approach each geminal contains a contribution from only one orbital that is occupied in a reference-state determinant (AP1roG; cf. Eq. (17)). The AP1roG wavefunction can be determined with mean-field-like quartic scaling ($O(P^2(K - P)^2)$, where $P = N/2$ is the number of electron pairs and K is the number of spatial orbitals in the one-electron basis set). The accuracy of AP1roG is breathtaking: in all cases we studied, including the strongly-correlated limit of the hydrogen atom chain, AP1roG gave energies that were virtually indistinguishable from doubly-occupied CI (DOCI), a factorial-scaling method that is known to be a suitable model for systems containing strongly correlated electrons.

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Table 1. The Hartree-Fock (HF) energy (including nuclear repulsion), E_{HF}, and the correlation energies of the doubly-occupied configuration interaction (DOCI) method, $\Delta_{\mathrm{DOCI}} = E_{\mathrm{DOCI}} - E_{\mathrm{HF}}$, DOCI with optimized orbitals, $\Delta_{\mathrm{DOCI}}^{\mathrm{opt}} = E_{\mathrm{DOCI}}^{\mathrm{opt}} - E_{\mathrm{HF}}$, and the antisymmetrized product of geminals with one distinct occupied reference orbital (AP1roG) with the DOCI optimized orbitals, $\Delta_{\mathrm{AP1roG}}^{\mathrm{opt}} = E_{\mathrm{AP1roG}}^{\mathrm{opt}} - E_{\mathrm{HF}}$. The last column lists the percentage of full-CI correlation energy that is obtained using AP1roG with these orbitals, $\%E_c = \Delta_{\mathrm{AP1roG}}^{\mathrm{opt}} / \Delta_{\text{full-CI}} \times 100\%$. All energies are given in milliHartree (1 mH = .0271 eV).

System	**Basis**	***R*[a]**	E_{HF}	Δ_{DOCI}	$\Delta_{\mathrm{DOCI}}^{\mathrm{opt}}$	$\Delta_{\mathrm{AP1roG}}^{\mathrm{opt}}$	$\%E_c$
2-electron systems							
H_2	STO-6G	2.0	-1056.430	-39.641	-39.641	-39.641	100.0%
H_2	6-31G**	2.0	-1088.267	-27.663	-38.860	-38.860	100.0%
He	6-31G**	–	-2855.160	-32.194	-32.205	-32.205	100.0%
HeH^+	6-31G**	2.0	-2901.915	-20.610	-36.596	-36.596	100.0%
4-electron systems							
Be	6-31G	–	-14566.764	-33.321	-46.264	-46.261	98.9%
He_2	6-31G**	4.0	-5709.176	-26.047	-64.147	-64.147	99.5%
He_2	6-31G**	200.0	-5710.321	-23.669	-64.409	-64.409	100.0%
10-electron systems							
Ne	6-31G	–	-128473.877	-36.151	-43.382	-43.384	37.4%
Ne	6-311G*	–	-128522.553	-69.721	-83.983	-83.979	36.2%
CH_4	STO-6G	2.05311	-40110.462	-25.004	-62.653	-62.646	78.2%
CH_4	6-31G	2.05311	-40180.502	-21.072	-75.953	-75.946	63.0%
$(H_2)_5$	STO-6G	2.0/2.5	-5244.349	-26.004	-162.208	-162.273	86.7%
$(H_2)_5$	STO-6G	2.0/3.0	-5264.465	-22.881	-182.020	-182.083	94.4%
$(H_2)_5$	STO-6G	2.0/4.0	-5278.399	-20.568	-195.507	-195.535	98.9%

a. *R* is the interatomic distance in atomic units of Bohr (1 Bohr = 5.292 x 10^{-11} m). For the linear chains of H_2 molecules, the two numbers stand for the intramolecular/intermolecular hydrogen-atom distances.

Figure 1. Graphical representation of the degree of flexibility in the coefficients of the various geminal-based wavefunctions considered in this paper and their relationship to each other. The antisymmetrized product of interacting geminals (APIG), antisymmetrized product of strongly orthogonal geminals (APSG), generalized valence bond/perfect pairing (GVB-PP), and antisymmetrized geminal power (AGP) wavefunctions are conventional approaches. The antisymmetrized product of rank-two reference-orbital geminals (APr2roG), antisymmetrized product of one reference-orbital geminals (AP1roG), and antisymmetrized product of rank-two geminals (APr2G) are proposed in this paper.

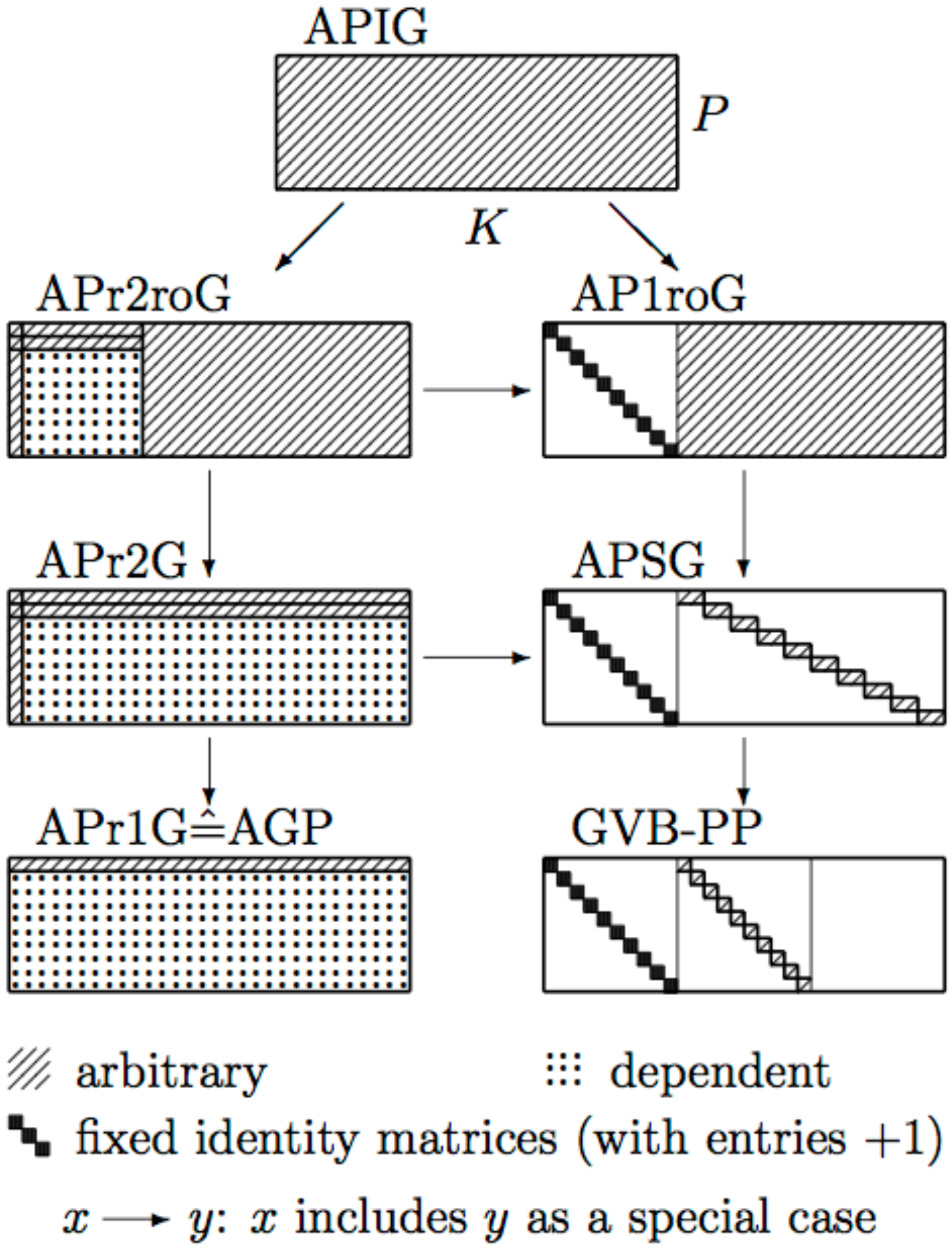


Figure 2. Bond stretching in an equidistant H_8 chain with internuclear distance *R* using an ANO-2s basis set.[86] (a) shows the absolute energy predicted by full CI, Hartree-Fock, MP2 (second order Moller-Plesset perturbation theory), and CCSD (coupled cluster with single and double excitations), DOCI with optimized orbitals, and AP1roG with the optimized orbitals from DOCI. (b) shows the fraction of the full CI correlation energy that is captured by these methods.

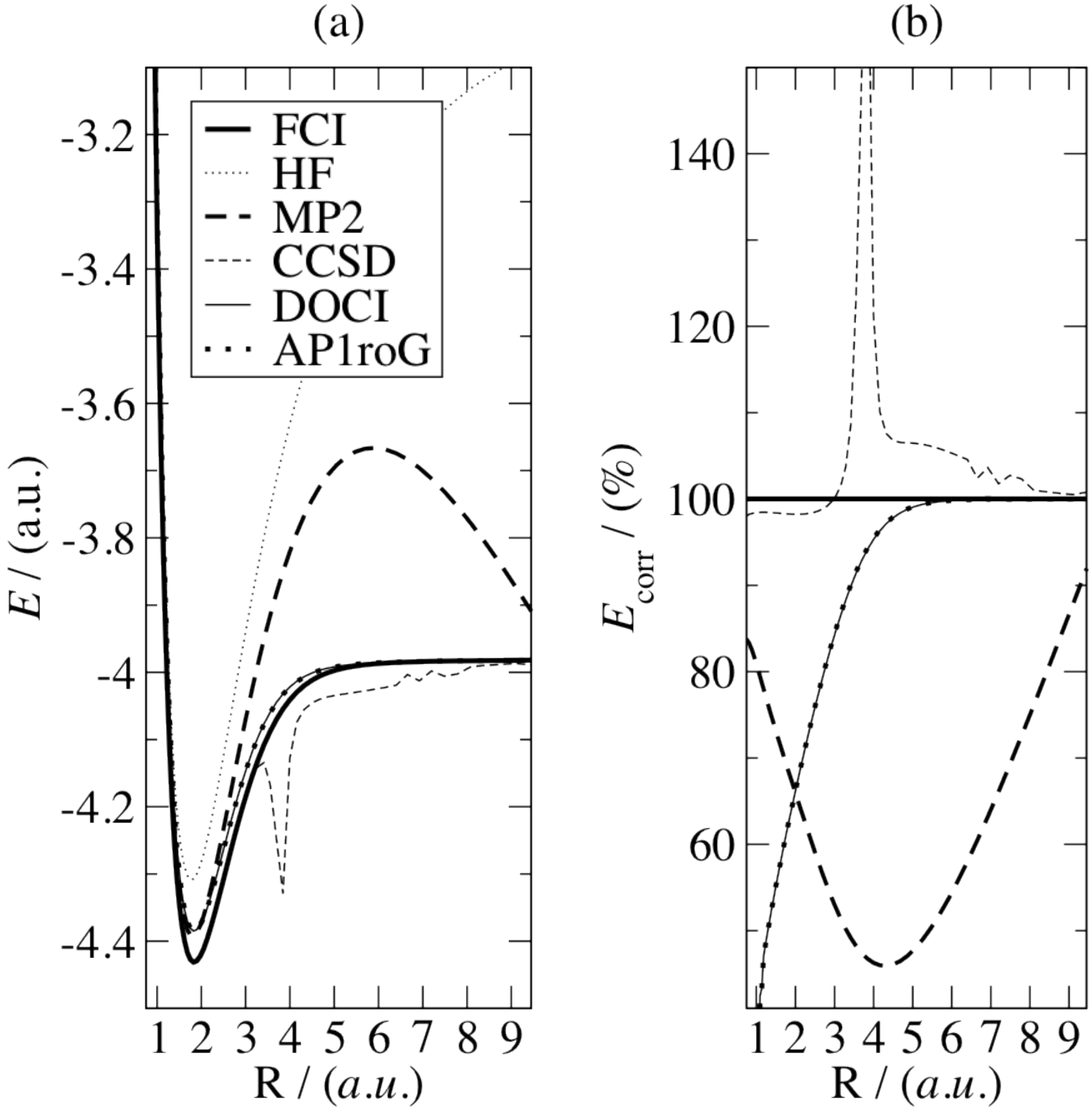


Figure 3. Comparison between AP1roG and related approaches for the same H_8 chains and basis set described in Figure 2. (a) shows the energy difference with respect to full CI for AP1roG and for the three coupled cluster approaches CCSD with canonical Hartree-Fock orbitals, CCSD with DOCI optimized orbitals (the same as for AP1roG), and CCD also using DOCI optimized orbitals. (b) shows the energy difference with respect to DOCI for AP1roG and for the two geminal approaches APSG and GVB-PP, all using DOCI optimized orbitals.

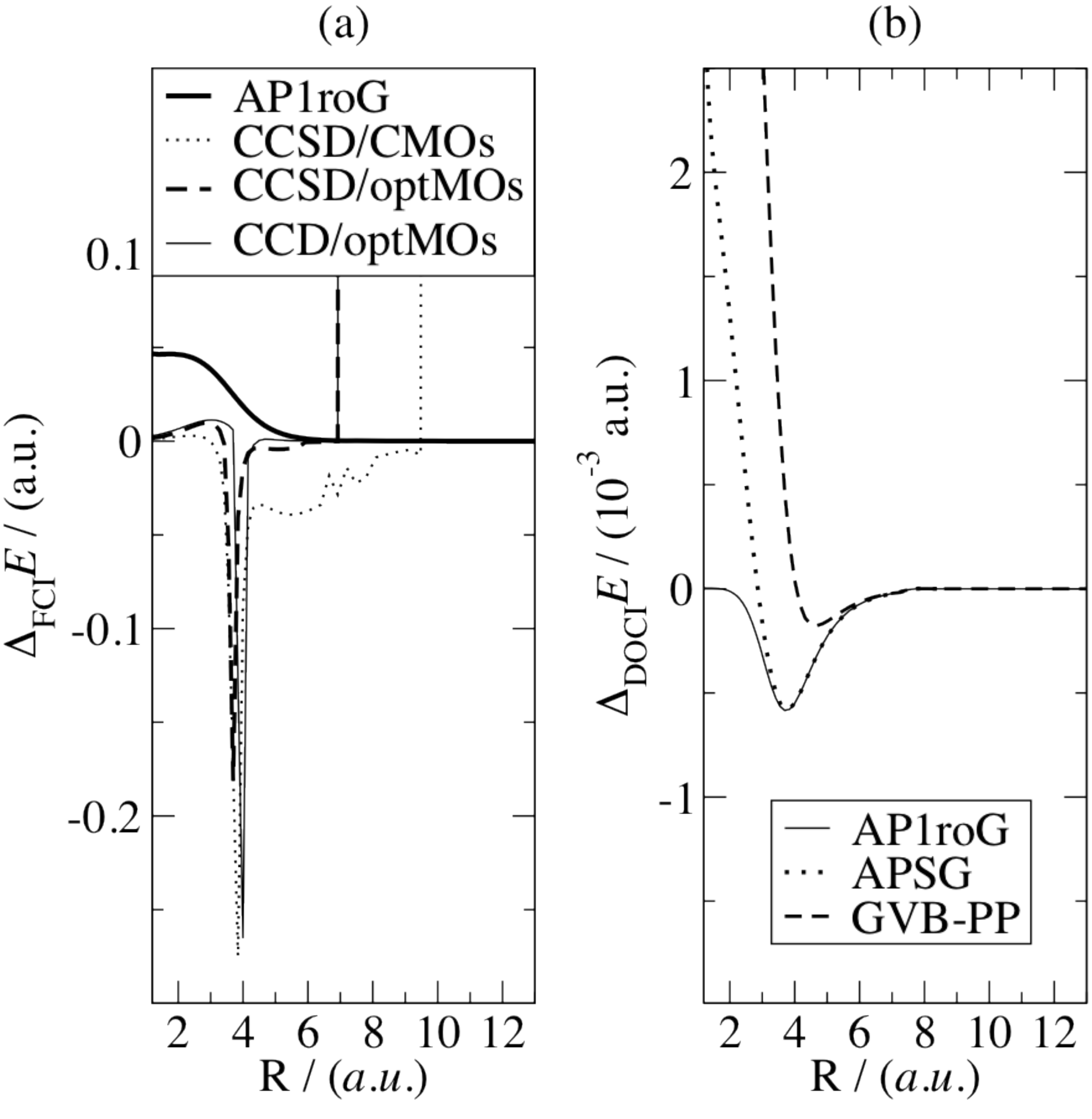
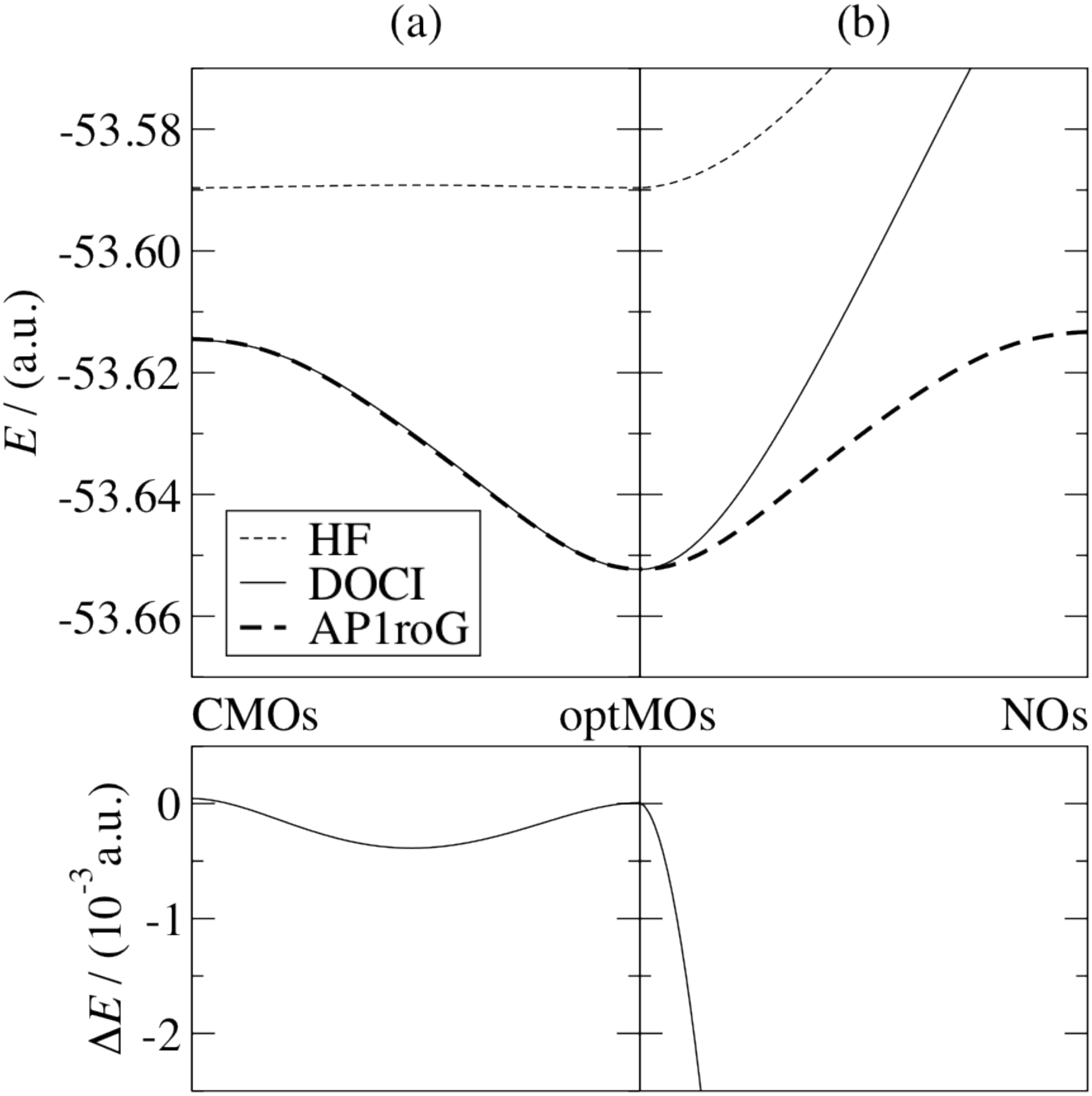


Figure 4. Orbital dependence of Hartree-Fock, DOCI, and AP1roG for CH_4 using the STO-6G basis set. The canonical Hartree-Fock orbitals on the left (a) and the proper natural orbitals from a full-CI calculation on the right (b) are gradually rotated towards the DOCI-optimized MOs located in the middle. The lower panel shows the energy difference $\Delta E = E_{\mathrm{AP1roG}} - E_{\mathrm{DOCI}}$.



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