

# Strongly orthogonal geminals: size-extensive and variational reference states

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## Abstract

Properties and some applications of strongly orthogonal geminals (APSG) are reviewed emphasizing the motivations for their use and their shortcomings. An overview presents some techniques capable of improving the APSG function.

## 1. INTRODUCTION

A characteristic feature of present-day quantum chemistry is the lack of simple though reliable models which were capable of describing specific phenomena or particular chemical processes. On the contrary, contemporary quantum chemistry focuses on ab initio methods, where the aim is to perform accurate computations without any reference to empirical data apart from universal constants of nature. While this goal is impressive, the present authors are convinced that as the size of the studied systems grows, there will be no way and no reason to compute everything from the very beginning, but appropriate models, based on previously gained knowledge, will have to be developed.

Forming effective models in chemistry, is not easy, however. This is because the systems we investigate have too many degrees of freedom to let us treating them by simple techniques, and too few degrees of freedom to treat them in a statistical manner.

In fact, there exist many qualitative models in chemistry, but these are usually too qualitative to form a basis of a reliable treatment. For example, the modeling of a polyatomic molecule by inner-shell cores and local, two-electron chemical bonds in the valence shell is inherently incorporated in the chemical thinking. Nevertheless, the mathematical description of this model is not at all trivial.

The importance of the model is electron pairs can be underlined by considering the following fact. Many polyatomic molecules can be meaningfully, albeit approximately, decomposed to 2-electronic units. From the pure mathematical point of view it appears that using electron trios or quadruples instead of electron pairs, one may acquire a more exact description. This is not necessarily the case, however. To give an example, the valence shell of the methane molecule cannot be viewed as an ensemble of electron quads without losing tetrahedral symmetry of the system. The seemingly more approximate description of the 4 electron pairs preserves the spatial symmetry of the molecule, facilitating a more correct picture.

In the past, several mathematical description of the two-electron chemical bonds have been proposed. At the Hartree-Fock level, the concept of localized molecular orbitals[1–21] became very fruitful, but such a description completely neglects the correlation among the electrons, at least at the zero order. Perturbation theory is then invoked to account for correlation effects, which has been effectively formulated[22–32] also in terms of localized

orbitals. Such a treatment, however, necessarily faces the difficulty to treat the correlation of the two strongly interacting electrons also perturbatively.

Correlation of close-lying electrons within a chemical bond can be included already at the zero order. This leads to the so-called geminal theories, the name 'geminal' coming from the two twin electrons of a bond describing a two-electron function, the geminal.

In this paper we briefly discuss geminal-type wave functions, list their advantages and shortcomings, and review a few technologies that aim to improve the approximation they provide.

## 2. THE NOTION OF GEMINALS

Consider first the Hartree-Fock determinant of a closed-shell system:

$$\Psi_{\text{HF}} = \underbrace{\phi_{1\uparrow}^+ \phi_{1\downarrow}^+}_{\phi_1^+} \underbrace{\phi_{2\uparrow}^+ \phi_{2\downarrow}^+}_{\phi_2^+} \dots \underbrace{\phi_{\frac{N}{2}\uparrow}^+ \phi_{\frac{N}{2}\downarrow}^+}_{\phi_{\frac{N}{2}}^+} |\text{vac}\rangle \quad (1)$$

Here we arranged each  $\beta$  orbital right after their  $\alpha$  counterpart, and indicated that they may form a Hartree-Fock pair.

A natural generalization of this wave function reads

$$\Psi_{\text{GEMINAL}} = \psi_1^+ \psi_2^+ \dots \psi_{\frac{N}{2}}^+ |\text{vac}\rangle \quad (2)$$

where

$$\psi_i^+ = \sum_{q=1}^{M_i} C_q^i \phi_{q\uparrow}^{i+} \phi_{q\downarrow}^{i+} \quad (3)$$

is a correlated singlet two-electron function, a geminal. Expansion coefficients  $C$  connect geminals to the underlying one-particle functions. Notation  $\phi_q^i$  expresses that, when constructing geminal  $i$ , functions  $\phi_q^i$  are selected only from a subspace of basis orbitals associated to geminal  $i$ . These subspaces are mutually exclusive[33], which is equivalent to restricting the geminals strongly orthogonal (*vide infra*).  $M_i$  is the dimension of the  $i$ -th subspace.

The geminal structure specified above is not the most general one, since

(i) the indices  $q$  of the  $\alpha$  and  $\beta$  functions are kept the same ("natural" geminals", see below), and

(ii) each geminal is kept singlet individually. Terms where two triplet geminals are coupled to form a 4-electron singlet, etc., would also be possible, but we do not discuss them here.

A more general form of a geminal could be written as

$$\psi_i^+ = \sum_{p,q=1}^{M_i} C_{pq}^i \phi_{p\uparrow}^{i+} \phi_{q\downarrow}^{i+}. \quad (4)$$

Here the coefficient matrix should be symmetric for singlet states, thus a unitary transformation within the  $i$ -th subspace can always be found bringing matrix  $\mathbf{C}$  to diagonal form. Accordingly, the special form of Eq.(3), as compared to the more general form Eq.(4), depends merely on the basis set. Deriving the first-order spatial density matrix from geminals Eq.(4), we obtain:

$$P_{pq}^i = \sum_{\sigma} \langle \psi_i | \phi_{p\sigma}^{i+} \phi_{q\sigma}^{i-} | \psi_i \rangle = 2 \sum_{r=1}^{M_i} C_{pr}^i C_{qr}^i, \quad (5)$$

where  $\sigma$  labels the spin. If, however the density matrix is evaluated from geminals of form (3), this expression is reduced to

$$P_{pq}^i = 2 \delta_{pq} C_p^i C_q^i, \quad (6)$$

thus the density matrices will also be diagonal. This justifies the term "natural geminal" if the form (3) is used.

An essential difference between the constituents of the HF and the APSG wave functions is manifested in the algebra the corresponding creation operators follow. In the Hartree-Fock case we have the common fermion anti-commutation relations:

$$\begin{aligned} [\phi_{i\sigma}^+, \phi_{k\sigma'}^+]_+ &= 0 \\ [\phi_{i\sigma}^-, \phi_{k\sigma'}^-]_+ &= 0 \\ [\phi_{i\sigma}^+, \phi_{k\sigma'}^-]_+ &= \delta_{ik} \delta_{\sigma\sigma'} \end{aligned} \quad (7)$$

which forms a Grassmann-algebra, while the geminal creation/annihilation operators obey much more complicated algebraic rules:

$$\begin{aligned} [\psi_i^+, \psi_k^+]_- &= 0 \\ [\psi_i^-, \psi_k^-]_- &= 0 \\ [\psi_i^-, \psi_k^+]_- &= \hat{Q}_{ik} \end{aligned} \quad (8)$$

Here operators  $\hat{Q}_{ik}$  can be specified as

$$\hat{Q}_{ik} = \delta_{ik} - \sum_p C_p^i C_p^k (\phi_{p\uparrow}^{k+} \phi_{p\uparrow}^{i-} + \phi_{p\downarrow}^{k+} \phi_{p\downarrow}^{i-}) \quad (9)$$

for natural orthogonal geminals satisfying

$$\langle \psi_i | \psi_k \rangle = \delta_{ik}. \quad (10)$$

The orthogonality condition (10) (called also as weak orthogonality, see e.g. [34, 35]) can be expanded in the natural basis (see expansion (3) for the geminals) as

$$\sum_p C_p^i C_p^k = \delta_{ik}, \quad (11)$$

whereas in the general basis the same weak orthogonality condition reads:

$$\sum_{pq} C_{pq}^i C_{pq}^k = \delta_{ik}. \quad (12)$$

If the geminals are strongly orthogonal[36–38], i.e., they are expanded in mutually exclusive subspaces of orthogonal basis functions[33, 39], this latter condition is simplified to

$$\sum_p C_{pr}^i C_{ps}^k = \delta_{ik} \quad \text{for all } r \text{ and } s, \quad (13)$$

since no common indices of basis functions for geminals  $i \neq k$  are possible in this case.

Rule (8) specifies commutation instead of the fermion anticommutation seen in (7). This is a trivial consequence of the fact that a geminal is composed of two electrons, so it can be considered as a bosonic system. It is quite important, however, that these bosons are not elementary, but composite particles, which is reflected by the appearance of  $\hat{Q}_{ik}$  which form a matrix of operators [40–42].

For some other important works dealing with composite particles relevant to quantum chemistry we refer to the papers[43–50]. Among these, the work by Ehrenfest and Oppenheimer [47] in 1931 is perhaps the first which applies the notion of composite particles.

Composite particles are often implicitly dealt with. For example, a successful model in the current research on ultra-cold atoms is the so-called Bose-Hubbard model, where alkali atoms are treated as composite particles, without discussing their internal structure[51].

Returning to geminals as two-electron composites, we see that dealing with a complicated algebra expressed by Eq. (9) is extremely difficult and substantial simplifications have to be made. This was the motivation behind introducing various orthogonality constraints[34, 35,

52] the stronger and most widespread being the condition of strong orthogonality[36–38]. Under strong orthogonality, the commutation relation is simplified to[39]

$$[\psi_i^-, \psi_k^+]_- = \hat{Q}_i \delta_{ik} \quad (14)$$

with

$$\hat{Q}_i = 1 - \sum_{m,n,l \in i} C_{ml}^i C_{nl}^i (\phi_{n\uparrow}^{i+} \phi_{m\uparrow}^{i-} + \phi_{n\downarrow}^{i+} \phi_{m\downarrow}^{i-}) = 1 - \frac{1}{2} \sum_{m,n \in i} P_{mn}^i (\phi_{n\uparrow}^{i+} \phi_{m\uparrow}^{i-} + \phi_{n\downarrow}^{i+} \phi_{m\downarrow}^{i-}) \quad (15)$$

in a general basis, while for natural geminals, using (6), this equation further simplifies to

$$\hat{Q}_i = 1 - \sum_{m \in i} (C_m^i)^2 (\phi_{m\uparrow}^{i+} \phi_{m\uparrow}^{i-} + \phi_{m\downarrow}^{i+} \phi_{m\downarrow}^{i-}). \quad (16)$$

To express that (14) is a tremendous simplification indeed, we recall that

$$\psi_i^- \psi_k^+ |\text{vac}\rangle = \delta_{ik} |\text{vac}\rangle \quad (17)$$

where we utilized that

$$\hat{Q}_i |\text{vac}\rangle = |\text{vac}\rangle.$$

In words, operators  $\psi_i^-$  can be considered as annihilators to  $\psi_k^+$ , resulting that Wick's theorem remains valid as far as one has a single occurrence of a geminal in the string studied.

The geminal wave function under the condition of strong orthogonality has been termed as APSG (antisymmetrized product of strongly orthogonal geminals), and was investigated by numerous authors[33, 36, 39, 42, 53–61].

### 3. CONNECTION BETWEEN APSG AND COUPLED CLUSTER

Several authors have pointed out that the APSG wave function (as any separable wave function satisfying the criterion of size-extensivity) can always be written in an exponential form[62–65]. The short derivation presented below indicates the generality of this statement.

First, let us rewrite a single natural geminal in exponential form:

$$\begin{aligned}
\psi_i^+ &= \sum_{q=1}^{M_i} C_q^i \phi_{q\uparrow}^{i+} \phi_{q\downarrow}^{i+} \\
&= C_1^i \phi_{1\uparrow}^{i+} \phi_{1\downarrow}^{i+} + \sum_{q=2}^{M_i} C_q^i \underbrace{\phi_{q\uparrow}^{i+} \phi_{q\downarrow}^{i+}}_{\phi_{q\uparrow}^{i+} \phi_{q\downarrow}^{i+} \phi_{1\downarrow}^{i-} \phi_{1\uparrow}^{i-} \phi_{1\uparrow}^{i+} \phi_{1\downarrow}^{i+}} \\
&= \left[ C_1^i + \sum_{q=2}^{M_i} C_q^i \underbrace{\phi_{q\uparrow}^{i+} \phi_{q\downarrow}^{i+} \phi_{1\downarrow}^{i-} \phi_{1\uparrow}^{i-}}_{\hat{t}_q} \right] \phi_{1\uparrow}^{i+} \phi_{1\downarrow}^{i+} \\
&= C_1^i \underbrace{\left[ 1 + \sum_{q=2}^{M_i} \frac{C_q^i}{C_1^i} \hat{t}_q \right]}_{e^{\hat{T}_i}} \phi_{1\uparrow}^{i+} \phi_{1\downarrow}^{i+},
\end{aligned}$$

where  $e^{\hat{T}_i}$  was possible to introduce since  $(\hat{T}_i)^2 = 0$  as well as all of its higher powers. Summarizing:

$$\psi_i^+ = C_1^i e^{\hat{T}_i} \phi_{1\uparrow}^{i+} \phi_{1\downarrow}^{i+}$$

The entire APSG wave function can therefore be rewritten as

$$\begin{aligned}
\Psi_{\text{APSG}} &= \psi_1^+ \psi_2^+ \dots |\text{vac}\rangle \\
&= \underbrace{C_1^1 C_1^2 \dots}_{C_0} \underbrace{e^{\hat{T}_1} e^{\hat{T}_2} \dots}_{e^{\hat{T}}} \underbrace{\phi_{1\uparrow}^{1+} \phi_{1\downarrow}^{1+} \phi_{1\uparrow}^{2+} \phi_{1\downarrow}^{2+} \dots}_{|\text{HF}\rangle} |\text{vac}\rangle \\
&= C_0 e^{\hat{T}} |\text{HF}\rangle,
\end{aligned} \tag{18}$$

where the  $|\text{HF}\rangle$  Fermi vacuum is a principal determinant, it coincides with the Hartree-Fock wavefunction if the  $\phi_i$  one-electron functions represent HF SCF orbitals. Coefficient  $C_0$  appears here to ensure the normalization of  $\Psi_{\text{APSG}}$  to unity, and it may be dropped if using intermediate normalization.

This derivation shows that the APSG Ansatz can be considered as a restricted CC wave function. Since only doubly excited states are involved in the natural geminal expansion

(3), APSG is a restricted CCD. Further, since in APSG theory the underlying one-electron orbitals are obtained variationally, the elimination of singles in the natural form (3) means that this wave-function is of Brueckner-type.

This observation is quite interesting, since, as shown in Fig. 1, CCSD method badly fails in describing triple bond dissociation. The APSG method, although dissociates to an incorrect spin state, provides a more attractive potential curve. This observation stimulated several recent studies by Head-Gordon and coworkers[65, 66].

#### 4. ADVANTAGES AND DISADVANTAGES OF THE APSG METHOD

The following points collect the most important *pros* of using the APSG wave function.

1. The wave function retains the formal simplicity of HF, cf. Eqs.(1)-(2).
2. Since each geminal describes a two-electron subunit, and the geminals tend to be localized automatically upon variational optimization in most cases, geminals may adequately represent two-electron chemical bonds<sup>1</sup>. Thereby, the theory is close to the chemists' way of thinking.
3. The mathematical description shows that geminals (chemical bonds) correspond to composite quasi-bosonic particles with an elegant algebra.
4. Owing to the strong orthogonality condition, geminals are easy to deal with.
5. The exponential cluster operator used by APSG relates it to the coupled cluster wave function, and ensures size-extensivity of the APSG approach.
6. The method properly describes single-bond dissociation.
7. Finally, the APSG energy is strict upper bound to the true energy.

Of course, the simplifications applied in APSG theory have serious consequences. We list below the most important ones.

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<sup>1</sup> Though often observed, localization of optimized geminals is not always the case - this may be system and basis set dependent.



1. Strong orthogonality is a too severe restriction, lifting it one may certainly obtain significantly lower energies[67–69]. At this price, however, the method loses its feasibility.
2. The APSG Ansatz is written in the so-called perfect-pairing approximation: electrons 1,2 form one pair, 3,4 form another one, etc., but no 1,3 pairs (e.g.) are considered. Therefore, no inter-geminal correlation is described by APSG.
3. The method does not describe properly multiple bond dissociation, since the separated products are of incorrect spin states.
4. The advantages listed above emerge only for the ground electronic state, while excited states are difficult to handle.
5. The method is appropriate only for molecules with a well-defined Lewis-structure, and hardly describes inherently delocalized objects such as benzene. Similarly, no collective phenomena are described by APSG.

A remedy of the last point is possible by allowing fragments composed of more than two electrons, in the sense of group function theory. Improving APSG to reduce the previous pitfalls is possible by several correction techniques. A few of them will be discussed in the following section.

## 5. IMPROVING GEMINALS

### 5.1. Geminal-CI

In the Geminal-CI approach[70], we use the APSG wave function as the reference state:

$$\Psi = \sum_K C_K \hat{O}_K |\text{APSG}\rangle, \quad (19)$$

where  $\hat{O}_K = p^+ i^-, p^+ q^+ i^- k^-, \dots$  etc. are the one-electron, two-electron etc. excitation operators. As discussed above, we can write the APSG reference in the following form:

$$|\text{APSG}\rangle = e^{\hat{T}} |\text{HF}\rangle \quad (20)$$

with the cluster operator

$$\hat{T} = \sum_i \sum_{q=2}^M \frac{C_q^i}{C_1^i} \phi_{q\uparrow}^{i+} \phi_{q\downarrow}^{i+} \phi_{1\uparrow}^{i-} \phi_{1\downarrow}^{i-},$$

where  $i$  orbitals belong to the reference determinant:

$$|\text{HF}\rangle = \prod_{i=1}^{N/2} \phi_{1\uparrow}^{i+} \phi_{1\downarrow}^{i+} |\text{vac}\rangle$$

Combining (19) and (20) the Schrödinger equation will be the following:

$$\sum_K \hat{H} e^{\hat{T}} \hat{O}_K |\text{HF}\rangle C_K = E \sum_K e^{\hat{T}} \hat{O}_K |\text{HF}\rangle C_K, \quad (21)$$

where we utilized the commutation relation  $[e^{\hat{T}}, \hat{O}_K] = 0$ .

Multiplying by  $\hat{O}_L^\dagger$  and projecting by  $\langle \text{HF} |$  we get the so called APSG-CI equations

$$\sum_K \underbrace{\langle \text{HF} | \hat{O}_L^\dagger \hat{H} e^{\hat{T}} \hat{O}_K | \text{HF} \rangle}_{\mathcal{H}_{LK}} C_K = E \sum_K \underbrace{\langle \text{HF} | \hat{O}_L^\dagger e^{\hat{T}} \hat{O}_K | \text{HF} \rangle}_{\mathcal{S}_{LK}} C_K, \quad (22)$$

which is a non-Hermitian generalized eigenvalue problem. (Alternatively, we could proceed from Eq. (21) with the projector  $\langle \text{HF} | \hat{O}_L^\dagger e^{-\hat{T}}$ , which would result in the diagonalization of the effective Hamiltonian  $e^{-\hat{T}} \hat{H} e^{\hat{T}}$  usual in Coupled Cluster theories.)

Numerical experience [70] shows that for total energies APSG-CISD energies fall in between CISD and CCSD in case of simple second-row hydrides, being usually closer to the latter. Size-consistency tests show that the method is fully size-consistent for processes when the supramolecular system is decomposed into two-electronic subsystems, e.g., the dissociation of a cluster of He atoms or hydrogen molecules. Size-consistency errors are also decreased for other cases (i.e., dissociating to non two-electronic fragments) as well, compared to the CISD error[70]. The APSG-CI method can also result in better energy differences. For numerical results on the dissociation of the HF molecule, the torsional rotation of H<sub>2</sub>O<sub>2</sub> and the umbrella inversion of NH<sub>3</sub> we refer to [70]. Eq. (22) is analogous to the EOM-CC equations[71–73], the difference being merely in the cluster operator  $\hat{T}$ . This might suggest that the APSG-CI method is capable of describing excitation energies. This expectation was not confirmed by numerical calculations, however (Kállay and Surján, unpublished).

## 5.2. Combining APSG with MP2

An extremely simple combination of the APSG method with standard MP2 calculation can be done by the following recipe:

1. Perform an APSG calculation, providing  $E_{APSG}$
2. Perform a standard MP2 with canonical MOs, providing  $E_{MP2}$
3. Perform a localized MP2 but only for intra-bond correlation, providing  $E_{MP2}^{\text{intra-bond}}$
4. Compute the energy as

$$E = E_{APSG} + E_{MP2} - E_{MP2}^{\text{intra-bond}}$$

Here item 3. requires a small and straightforward modification of a localized MP2 routine[25, 26], identifying and omitting intra-pair contributions. In spite of a few promising results (see e.g. Table I), a broader numerical study revealed that this correction scheme is insufficient in most cases (M. Kobayashi, Á. Szabados and P.R. Surján, unpublished).

## 5.3. Perturbation corrections to APSG

A more robust correction is obtained if considering the APSG as zero-order approximation and expanding the exact wave-function as a perturbation series. Among several possibilities for a zero-order operator behind such an approach, it is most appealing to use a zero-order containing the intra-geminal two-body terms of the Hamiltonian and a mean-field term corresponding to inter-geminal interaction. Such a zero-order – first suggested by Dyall[74] – incorporates all the interactions accounted for by the APSG function and leads to a PT formalism adapted especially for the geminal wave-function. While the two-body nature of the zero-order operator presents some computational difficulties, the results of such a theory are remarkably good already at second order[75].

Another sophisticated perturbation theory to correct geminal wave functions was proposed by Rassolov[76]. Yet another second order correction to the perfect pairing approximation was done in Ref.[77].

It is also possible to apply a less demanding correction scheme to the APSG function. This is provided e.g. by multi-configuration perturbation theory[78, 79] (MCPT) which is a

general PT formulation, applicable to any zero order wave-function. The theory considers a multiconfigurational wave-function – APSG for instance – and all excited determinants to provide a basis in the configurational space. At the same time, these functions are eigenfunctions of the zero-order Hamiltonian, facilitating a simple inversion of the reduced resolvent. This leads to a transparent formulation and coding of the PT expressions.

One determinant of APSG is regarded as "ground state" and it is not present among the functions forming the basis. This is the pivotal determinant, denoted by HF in Eq.(18). Provided that  $C_0$  is nonzero, the basis

$$|\Psi_{\text{APSG}}\rangle, |K\rangle, K = 1, \dots \quad (23)$$

is complete in the CI space, it is however non-orthogonal. To deal with this situation, the reciprocal set to the functions (23) is constructed, which is formed by the tilded functions

$$\langle\tilde{\Psi}_{\text{APSG}}|, \langle\tilde{K}|, K = 1, \dots .$$

Remarkably, no numerical procedure is needed to obtain the reciprocal set. Due to the simple structure of the overlap matrix, the above functions can be given in the closed form

$$\begin{aligned} \langle\tilde{\Psi}_{\text{APSG}}| &= \frac{1}{C_0} \langle\text{HF}| \\ \langle\tilde{K}| &= \langle K| - \frac{C_K}{C_0} \langle\text{HF}| \end{aligned}$$

With the use of these functions, a non-hermitian zero-order can be written down in the spectral form

$$\hat{H}^0 = E_0 |\Psi_{\text{APSG}}\rangle \langle\tilde{\Psi}_{\text{APSG}}| + \sum_{K=1} E_K |K\rangle \langle\tilde{K}| . \quad (24)$$

Here

$$E_0 = \langle\tilde{\Psi}_{\text{APSG}}|\hat{H}|\Psi_{\text{APSG}}\rangle \quad (25)$$

is the energy of the reference state. This is not the APSG energy, which would be given by the symmetrical expression  $E_{\text{APSG}} = \langle\Psi_{\text{APSG}}|\hat{H}|\Psi_{\text{APSG}}\rangle$ . The deviation of  $E_0$  from  $E_{\text{APSG}}$  is however typically slight in numerical terms. Values  $E_K$  in expression (24) of  $\hat{H}^0$  are adjustable parameters of the theory.

Since functions  $|\Psi_{\text{APSG}}\rangle$  and  $|K\rangle$  are eigenfunctions to  $\hat{H}^0$  from the right, it is most practical to expand PT corrections to the zero-order function on this basis. Tilded functions

being eigenfunctions to  $H^0$  from the left, the well known sum over states form is valid for the PT terms. One has e.g.

$$|\Psi^1\rangle = - \sum_{K=1} |K\rangle \frac{\langle \tilde{K} | \hat{W} | \Psi_{\text{APSG}} \rangle}{E_K - E_0}$$

at first order, with  $\hat{W} = \hat{H} - \hat{H}^0$ . This gives rise to the second order energy expression

$$E^2 = - \sum_{K=1} \frac{\langle \tilde{\Psi}_{\text{APSG}} | \hat{W} | K \rangle \langle \tilde{K} | \hat{W} | \Psi_{\text{APSG}} \rangle}{E_K - E_0}$$

Note, that  $E^1 = 0$ , due to the choice Eq.(25).

Various possible ways of defining zero-order excited state energies,  $E_K$  lead to various partitionings within the MCPT framework[78–80]. It is usual to consider the form

$$E_K = E_0 + \Delta_K,$$

where  $\Delta_K$  is the energy difference appearing in PT denominators. It may be constructed as sums and differences of suitable one-particle energies, which are e.g. diagonal elements of the generalized Fockian present in MCSCF theory. This partitioning was termed Davidson-Kapuy (DK), being in analogy with early studies of these authors on PT, formulated in terms of localized orbitals[23, 81]. Alternatively, one-particle energies may be taken as ionization potentials and electron affinities calculated with  $\Psi_{\text{APSG}}$ [82]. It is also possible to make the choice  $E_K = \langle \tilde{K} | \hat{H} | K \rangle$ , giving rise to a generalized Epstein-Nesbet (EN) partitioning[83, 84]. Numerical experience shows that the error of second order energies is somewhat smaller in EN than in DK partitioning. On the other hand, size-consistency of the second order expression may be ensured in the latter but not in the former[79]. An account on different partitionings in MCPT is given in Ref.[80].

As the above discussion indicates, MCPT framework is a collective term, referring to several different methods, arising e.g. from different partitionings. Apart from the flexibility of the partitioning, variation of other ingredients of the theory have been also explored. The original formulation e.g. works with an alternative set of basis function in the CI space[78]. These are obtained by a Schmidt-orthogonalization of excited determinants to  $\Psi_{\text{APSG}}$ , and still possess reciprocal vectors expressible in closed form. By another modification of the formulae, it is possible to consider a non-diagonal zero-order Hamiltonian in the MCPT framework[85]. This study was motivated by the fact that a proper formulation of the

Møller-Plesset (MP) partitioning[86] requires to consider the generalized Fockian as zero-order, which is however a non-diagonal one in the general case. Solution for the first-order wave-function proceeds by iterating the linear system of equations. For practical applicability of the approach, it is crucial to keep the expansion of the first order venation of limited length. Starting from the APSG function, it was found satisfactory to include determinants at most doubly excited with respect the pivotal one. Numerical experience obtained on dissociation curves of this MP-MCPT theory shows nice agreement with the more elaborate PT formulation applying Dyllal’s Hamiltonian[85].

#### 5.4. Constant Denominators in Perturbation Theory

The nice properties of the APSG function detailed in Section 4 encourage the testing of PT treatments less elaborate than those of Section 5.3. Studies with simpler correction schemes are motivated by the idea that the essential correlation effects of a molecular system are captured by APSG. Hence, the negligible remainder could be possible to obtain by a simpler formalism just as well.

In order to arrive at a such an approximation scheme, we start from Löwdin’s exact implicit energy formula, which for an arbitrary reference function  $\Phi$  reads as

$$1 = \langle \Phi | \hat{H} (E - \hat{P} \hat{H})^{-1} | \Phi \rangle$$

In the following, we will substitute the APSG function for  $\Phi$ . The implicit energy formula can be obtained by the partitioning technique[87, 88], introducing the projector of the reference space

$$\hat{O} = |\Psi_{\text{APSG}}\rangle \langle \Psi_{\text{APSG}}|$$

and its orthogonal complement

$$\hat{P} = 1 - \hat{O} .$$

We proceed by partitioning the Hamiltonian, and choosing a zero-order operator with a common, averaged excited state energy, denoted by  $\nu$ :

$$\hat{H}^0 = E_0 \hat{O} + \nu \hat{P} . \tag{26}$$

This simple form of  $\hat{H}^0$  was first advocated by Unsöld and the resulting PT expansions were studied in more detail by Cullen et al.[89, 90]. The zero-order ground state energy,  $E_0$  in

Eq.(26) is in principle arbitrary, we will now assume that it equals the APSG energy

$$E_0 = \langle \Psi_{\text{APSG}} | \hat{H} | \Psi_{\text{APSG}} \rangle = \langle \hat{H} \rangle.$$

In what follows, expectation values taken with  $\Psi_{\text{APSG}}$  will be denoted by  $\langle \cdot \rangle$  for brevity.

Making use of

$$H = \hat{H}^0 + V$$

and Eq.(26), the implicit energy formula can be rewritten as

$$1 = \langle \hat{H}(E - \nu\hat{P} - \hat{P}\hat{V})^{-1} \rangle,$$

where we used the orthogonal character of the projectors ( $\hat{O}\hat{P} = 0$ ). The well-known identity

$$(\hat{A} - \hat{B})^{-1} = \hat{A}^{-1} + \hat{A}^{-1}\hat{B}(\hat{A} - \hat{B})^{-1} = \hat{A}^{-1} + \hat{A}^{-1}\hat{B}\hat{A}^{-1} + \hat{A}^{-1}\hat{B}\hat{A}^{-1}\hat{B}\hat{A}^{-1} + \dots \quad (27)$$

with  $\hat{A} = E - \nu\hat{P}$  and  $\hat{B} = \hat{P}\hat{V}$  gives

$$1 = \langle \hat{H}(E - \nu\hat{P})^{-1} \rangle + \langle \hat{H}(E - \nu\hat{P})^{-1}\hat{P}\hat{V}(E - \nu\hat{P})^{-1} \rangle + \mathcal{O}(3). \quad (28)$$

Furthermore, based on expression (27) one has

$$(E - \nu\hat{P})^{-1} | \Psi_{\text{APSG}} \rangle = \frac{1}{E} | \Psi_{\text{APSG}} \rangle,$$

which converts the implicit expression (28) into the form

$$E = \langle \hat{H} \rangle + \langle \hat{H}(E - \nu\hat{P})^{-1}\hat{P}\hat{V} \rangle + \mathcal{O}(3)$$

Expanding now the energy into a Taylor-series and collecting terms of the same order, up to order two, we see that only  $E_0$  can contribute to the second term on the right:

$$E = E_0 + \langle \hat{H}(E_0 - \nu\hat{P})^{-1}\hat{P}\hat{V} \rangle + \mathcal{O}(3)$$

The inverse operator appearing in the second-order term can be expressed as

$$(E_0 - \nu\hat{P})^{-1} = (E_0\hat{O} + E_0\hat{P} - \nu\hat{P})^{-1} = \frac{\hat{O}}{E_0} + \frac{\hat{P}}{E_0 - \nu}.$$

leading to the expression

$$E = E_0 + \frac{\langle \hat{V}\hat{P}\hat{V} \rangle}{E_0 - \nu} + \mathcal{O}(3). \quad (29)$$

This second order energy bears direct relationship with the original MCPT formulation discussed previously[78]. In fact, Eq.(29) can be obtained by substituting the energy denominators of this MCPT expression by the common value  $E_0 - \nu$ .

The averaged zero-order excited state energy,  $\nu$  in Eq.(29) is still unspecified. It can be considered as a single parameter of the theory, which should be set to optimize the performance. Such a condition was suggested by Feenberg[91, 92], who required the vanishing of the third order of the above expansion, i.e.

$$\frac{\langle \hat{V} \hat{P} (\hat{V} - \langle \hat{V} \rangle) \hat{P} \hat{V} \rangle}{(E_0 - \nu)^2} = 0 \quad (30)$$

Note that the numerator does depend on  $\nu$  through  $\hat{V} = \hat{H} - \hat{H}^0 = \hat{H} - E_0 \hat{O} - \nu \hat{P}$ . Since

$$\langle \hat{V} \hat{P} \hat{V} \hat{P} \hat{V} \rangle = \langle \hat{H} \hat{P} \hat{H} \hat{P} \hat{H} \rangle - \nu \langle \hat{H} \hat{P} \hat{H} \rangle = \langle \hat{H}^3 \rangle_c + E_0 \langle \hat{H}^2 \rangle_c - \nu \langle \hat{H}^2 \rangle_c,$$

and  $\langle \hat{V} \rangle = 0$ , Feenberg's condition results

$$\nu = E_0 + \frac{\langle \hat{H}^3 \rangle_c}{\langle \hat{H}^2 \rangle_c} \quad (31)$$

for the averaged excited-state energy, with  $\langle \cdot \rangle_c$  referring to connected moments[93] e.g.

$$\langle \hat{H}^2 \rangle_c = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \quad (32)$$

$$\langle \hat{H}^3 \rangle_c = \langle \hat{H}^3 \rangle - 3\langle \hat{H} \rangle^2 \langle \hat{H} \rangle + 2\langle \hat{H} \rangle^3 \quad (33)$$

Remarkably, the PT expansion arising from choice (31) agrees completely with the connected moment expansion (CMX) derived earlier, based on the Horn-Weinstein functional[94]. The very same, CMX expansion is also recovered, if requiring the stationary condition[88]

$$\frac{d}{d\nu} \left( \frac{\langle \hat{V} \hat{P} \hat{V} \rangle}{E_0 - \nu} + \frac{\langle \hat{V} \hat{P} (\hat{V} - \langle \hat{V} \rangle) \hat{P} \hat{V} \rangle}{(E_0 - \nu)^2} \right) = 0$$

instead of Feenberg's condition (30).

An example illustrating the performance of the CMX expansion is presented in Figure 2, showing the symmetric dissociation of the H<sub>2</sub>O molecule. As observable in the Figure, the the CMX corrected curves run roughly in parallel with the reference curve, while getting gradually closer to the full CI curve. Since the Hartree-Fock wave-function yields too large force constants, it is less advantageous to apply CMX to this reference function. The APSG function on the other hand produces a much improved shape for the potential curve. As the



bottom panel of Fig. 2 reflects, the curve shape is practically conserved but total energies are significantly improved if adding the CMX corrections computed with this reference function.

Table II. shows the total energies for a Be atom calculated in 6-311G\*\* basis set at the Hartree-Fock, MP2, APSG and FCI levels in comparison with the CMX2 and CMX3 corrected energies.

## 6. CONCLUSION

The advantages of the APSG wave function listed in Section 4 make them challenging candidates for developing a *geminal model chemistry*, a point emphasized by Rassolov[76, 95–97]. The disadvantages listed there stimulated developments of several correction schemes. Some of these have been reviewed in the present paper. Much work has yet to be done, however, to establish a robust and general geminal-based method facilitating black-box calculations. On the other hand, the geminal approach is indeed suitable to perform calculations on large systems where one is focused on locally broken chemical bonds or similar effects needing high-level account of local correlation. In these cases, the possibility of a specific treatment may be more important than black-box generality.

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- [1] S.F. Boys. *Rev. Mod. Phys.*, 32:296, 1960.
  - [2] C. Edmiston and K. Ruedenberg. *Rev.Mod.Phys.*, 35:457, 1963.
  - [3] C. Edmiston and K. Ruedenberg. *J. Chem. Phys.*, 43:S97, 1965.
  - [4] Z.B. Maksić (ed.). *Theoretical Models in Chemical Bonding, parts 1-4*. Springer, Heidelberg, 1990.

- [5] V. Magnasco and A. Perico. *J. Chem. Phys.*, 47:971, 1967.
- [6] V. Magnasco and A. Perico. *J. Chem. Phys.*, 48:800, 1968.
- [7] J. Pipek and P. G. Mezey. *J. Chem. Phys.*, 90:4916, 1989.
- [8] W. England, L. S. Salmon, and K. Ruedenberg. *Topics in Current Chemistry*, 23:31, 1971.
- [9] H. Weinstein and R. Pauncz. *Advances in Atomic and Molecular Physics*, 7:97, 1971.
- [10] O. Matsuoka. *J. Mol. Struct. (THEOCHEM)*, 230:67, 1991.
- [11] D. Maynau, S. Evangelisti, N. Guihery, C. J. Calzado, and J.-P. Malrieu. *J. Chem. Phys.*, 116:10060, 2002.
- [12] E. Gianinetti, M. Raimondi, and E. Tornaghi. *Int. J. Quantum Chem.*, 60:157, 1996.
- [13] A. Famulari, E. Gianinetti, M. Raimondi, and M. Sironi. *Int. J. Quantum Chem.*, 69:151, 1998.
- [14] James J. P. Stewart. *Int. J. Quantum Chem.*, 58:133, 1996.
- [15] J. P. Daudey. *Chem. Phys. Letters*, 24:547, 1974.
- [16] T. L. Gilbert. in: *Molecular Orbitals in Chemistry, Physics and Biology*, page 405. Academic, New York, 1964.
- [17] J. Rubio, A. Povill, J.-P. Malrieu, and P. Reinhardt. *J. Chem. Phys.*, 107:10044, 1997.
- [18] P. R. Surján and I. Mayer. *Theor. Chim. Acta*, 59:603, 1981.
- [19] P. R. Surján, I. Mayer, and M. Kertész. *J. Chem. Phys.*, 77:2454, 1982.
- [20] I. Mayer and P. R. Surján. *J. Chem. Phys.*, 80:5649, 1984.
- [21] P. R. Surján, M. Révész, and I. Mayer. *J. Chem. Soc. Faraday II*, 77:1129, 1981.
- [22] E. Kapuy, F. Bartha, F. Bogár, and C. Kozmutza. *Theor. Chim. Acta*, 72:337, 1987.
- [23] E. Kapuy, F. Bartha, F. Bogár, Z. Csépes, and C. Kozmutza. *Int. J. Quantum Chem.*, 38:139, 1990.
- [24] E. Kapuy, Z. Csépes, and C. Kozmutza. *Int. J. Quantum Chem.*, 23:981–990, 1983.
- [25] P. Pulay and S. Saebø. *Theor. Chim. Acta*, 69:357, 1986.
- [26] S. Saebø and P. Pulay. *J. Chem. Phys.*, 86:914, 1987.
- [27] Georg Hetzer, Martin Schütz, Hermann Stoll, and Hans-Joachim Werner. *J. Chem. Phys.*, 113:9443, 2000.
- [28] Jan Almlöf. *Chem. Phys. Letters*, 176:319, 1991.
- [29] P.Y. Ayala and G.E. Scuseria. *J. Chem. Phys.*, 110:3660–3671, 1999.
- [30] Péter R. Surján. *Chem. Phys. Letters*, 406:318–320, 2005.

- [31] S.Diner, J.-P.Malrieu, and P.Clavery. *Theor. Chim. Acta*, 13:1,18, 1969.
- [32] J.-P.Malrieu in: *Semiempirical Methods in Electronic Structure Calculation*, Ed. G.A.Segal. Plenum, New York, 1977.
- [33] T. Arai. *J. Chem. Phys.*, 33:95, 1960.
- [34] S. Wilson. *J. Chem. Phys.*, 64:1692, 1976.
- [35] P. Cassam-Chenai. *Phys. Rev. A*, 77:032103, 2008.
- [36] A. C. Hurley, J. Lennard-Jones, and J. A. Pople. *Proc. Roy. Soc. (London)*, A220:446, 1953.
- [37] R.G. Parr, F.O. Ellison, and P.G. Lykos. *J. Chem. Phys.*, 24:1106, 1956.
- [38] R.McWeeny. *Proc. Roy. Soc. (London)*, A253:242, 1959.
- [39] P. R. Surján. *Topics in current chemistry*, 203:63–88, 1999.
- [40] C. Valdemoro. *Phys. Rev. A*, 31:2114, 1985.
- [41] C. Valdemoro. *Phys. Rev. A*, 31:2123, 1985.
- [42] P. R. Surján. in: *Theoretical Models of Chemical Bonding*, volume 2, The Concept of the Chemical Bond, Z.B.Maksić (ed.), page 205. Springer, Berlin–Heidelberg, 1990.
- [43] M. Girardeau. *J. Math. Phys.*, 4:1096, 1963.
- [44] M. D. Girardeau. *Phys. Rev. Letters*, 27:1416, 1971.
- [45] M. D. Girardeau. *Int. J. Quantum Chem.*, 17:25, 1980.
- [46] V. Kvasnička. *Czech. J. Phys.*, B32:947, 1982.
- [47] P. Ehrenfest and J.R. Oppenheimer. *Phys. Rev. Letters*, 37:333, 1931.
- [48] M. D. Girardeau. *J. Math. Phys.*, 11:681, 1970.
- [49] M. D. Girardeau. *J. Math. Phys.*, 12:1799, 1971.
- [50] A.Y. Sakakura. *Phys. Rev.*, 37:822, 1971.
- [51] F. Dalfovo, S. Giorgini, L.P. Pitaevskii, and S. Stringari. *Rev. Mod. Phys.*, 71:463, 1999.
- [52] P. Cassam-Chenai and V. Rassolov. *Chem. Phys. Letters*, 487:147 – 152, 2010.
- [53] A. C. Hurley. *Electron correlation in small molecules*. Academic, New York, 1976.
- [54] J. M. Parks and R. G. Parr. *J. Chem. Phys.*, 28:335, 1957.
- [55] W. Kutzelnigg. *J. Chem. Phys.*, 40:3640, 1964.
- [56] K.J. Miller and K. Ruedenberg. *J. Chem. Phys.*, 48:3444, 1968.
- [57] E. Kapuy. *Acta Phys. Hung.*, 11:97, 1960.
- [58] E. Kapuy. *Theor. Chim. Acta*, 3:379, 1965.
- [59] E. Kapuy. *J. Chem. Phys.*, 44:956, 1966.

- [60] E. Kapuy and N. March. *J. Math. Phys.*, 8:1915, 1967.
- [61] E. Kapuy. *Acta Phys. Hung.*, 24:307, 1968.
- [62] I. I. Ukrainskii. *Theor. Math. Phys.*, 32:816, 1978.
- [63] John Cullen. *Chem. Phys.*, 202:217–229, 1996.
- [64] Troy Van Voorhis and Martin Head-Gordon. *Chem. Phys. Letters*, 317:575–580, 2000.
- [65] Troy Van Voorhis and Martin Head-Gordon. *J. Chem. Phys.*, 115(17):7814–7821, 2001.
- [66] Troy Van Voorhis and Martin Head-Gordon. *J. Chem. Phys.*, 117:9190–9201, 2002.
- [67] D.M. Silver. *J. Chem. Phys.*, 50:5108, 1969.
- [68] D.M. Silver. *J. Chem. Phys.*, 52:299, 1070.
- [69] V.A. Nicely and J.F.Harrison. *J. Chem. Phys.*, 54:4363, 1971.
- [70] M. Kállay and P. R. Surján. *Chem. Phys. Letters*, 312:221, 1999.
- [71] J.Geertsen, M. Rittby, and R. J. Bartlett. *Chem. Phys. Letters*, 164:57, 1989.
- [72] J. F. Stanton and R. J. Bartlett. *J. Chem. Phys.*, 98:7029, 1993.
- [73] J. D. Watts and R. J. Bartlett. *J. Chem. Phys.*, 101:3073, 1994.
- [74] K.G. Dyall. *J. Chem. Phys.*, 102:4909, 1995.
- [75] E. Rosta and P. R. Surján. *J. Chem. Phys.*, 116:878–890, 2002.
- [76] V. A. Rassolov, F. Xu, and S. Garashchuk. *J. Chem. Phys.*, 120:10385–10394, 2004.
- [77] G.J.O. Beran, M. Head-Gordon, and S.R. Gwaltney. *J. Chem. Phys.*, 124:114107, 2006.
- [78] Z. Rolik, Á. Szabados, and P. R. Surján. *J. Chem. Phys.*, 119:1922, 2003.
- [79] Ágnes Szabados, Zoltán Rolik, Gábor Tóth, and Péter R. Surján. *J. Chem. Phys.*, 122:114104, 2005.
- [80] P.R. Surján, Z. Rolik, Á. Szabados, and D. Kóhalmi. *Ann. Phys. (Leipzig)*, 13:223–231, 2004.
- [81] E. R. Davidson. *J. Chem. Phys.*, 57:1999, 1972.
- [82] Á. Szabados and P. Nagy. *J. Phys. Chem. A*, 115:523–534, 2011.
- [83] P.S. Epstein. *Phys. Rev.*, 28:695, 1926.
- [84] R.K. Nesbet. *Proc. Roy. Soc. (London)*, A230:312, 1955.
- [85] M. Kobayashi and Á. Szabados and H. Nakai and P. R. Surján. *J. Chem. Theory. Comput.*, 6:2024–2034, 2010.
- [86] C. Møller and M.S. Plesset. *Phys. Rev.*, 46:618, 1934.
- [87] P.-O Löwdin. *J. Mol. Struct. (THEOCHEM)*, 165:177, 1988.
- [88] P. R. Surján and Á. Szabados. *Int. J. Quantum Chem.*, 90:20–26, 2002.

- [89] J.M. Cullen. *Int. J. Quantum Chem.*, 33:497–527, 1982.
- [90] J.M. Cullen and M.C. Zerner. *Theor. Chim. Acta*, 61:203–226, 1982.
- [91] E. Feenberg. *Phys. Rev.*, 103:1116, 1956.
- [92] P. Goldhammer and E. Feenberg. *Phys. Rev.*, 101:1233, 1955.
- [93] D. Horn and M. Weinstein. *Phys. Rev. D*, 30:1256–1270, 1984.
- [94] J. Cioslowski. *Phys. Rev. Lett.*, 58:83, 1987.
- [95] V. A. Rassolov. *J. Chem. Phys.*, 117:5978, 2002.
- [96] V. A. Rassolov and F Xu. *J. Chem. Phys.*, 126:234112, 2007.
- [97] V. A. Rassolov and F Xu. *J. Chem. Phys.*, 127:044104, 2007.

TABLE I: Inversion barrier of the H<sub>2</sub>O and NH<sub>3</sub> molecule, computed in 6-311G\*\* basis set. Abbreviation APSG-MP2 refers to the procedure described in Section 5.5.2.

Method	Barrier [kJ/mol]	
	H <sub>2</sub> O	NH <sub>3</sub>
APSG	163.30	29.47
APSG-MP2	148.54	25.69
MP2	145.85	24.39
CCSD	147.99	25.31
CCSDT	148.89	25.71

TABLE II: Total energies for the Be atom in 6-311G\*\* basis set in atomic units.

	$E_{tot} / E_h$
HF-SCF	-14.57187
MP2	-14.59847
HF + CMX2	-14.58179
HF + CMX3	-14.58789
APSG	-14.61734
APSG + CMX2	-14.63210
APSG + CMX3	-14.63323
FCI	-14.63338

FIG. 1: Dissociation curve of the  $N_2$  molecule obtained in STO-3G basis set by the APSG, CCSD and full CI methods.

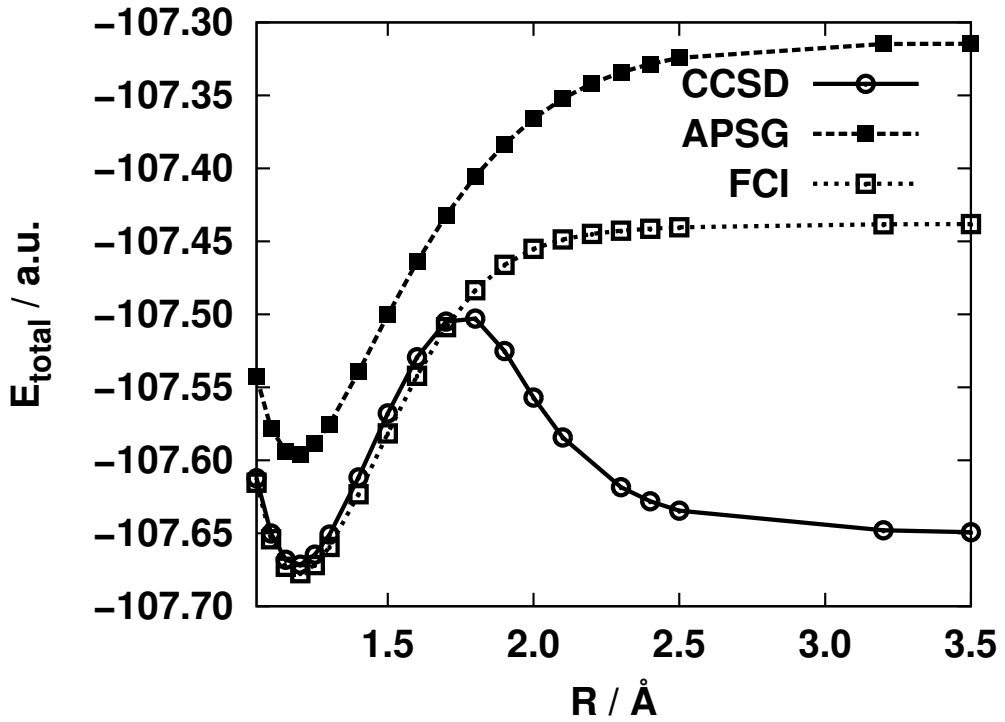


FIG. 2: Symmetric dissociation of the water molecule obtained by low-order terms of the CMX expansion, computed with the Hartree-Fock and the APSG function. The basis set is 6-31G, angle  $\angle(\text{H},\text{O},\text{H})$  is fixed at  $104.5^\circ\text{C}$ . Energy error displayed in the bottom panel is computed as  $E_{\text{total}} - E_{\text{FCI}}$ .

