Seniority based Energy Renormalization Group (Ω -ERG) Approach in Quantum Chemistry: Initial Formulation and Application to Potential Energy Surfaces

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Abstract: This investigation combines the concept of the seniority number Ω (defined as the total number of singly occupied orbitals in a determinant) with the energy renormalization group (ERG) approach to obtain the lowest-energy electronic states on molecular potential energy surfaces. The proposed Ω -ERG method uses Slater determinants that are *ordered* according to seniority number Ω in ascending order. In the Ω -ERG procedure, *the active system* consists of M (N-electron) states and K additional complement (N-electron) states (*complement-system*). Among the M states in the active system the lowest-energy m states represent target states of interest (*target-states*), thus $m \leq M$. *The environment* consists of Full Configuration Interaction (FCI) determinants that represent *a reservoir* from which the complement-states K are being selected. The goal of the Ω -ERG procedure is to obtain lowest-energy target states m of FCI quality in an iterative way at a reduced computational cost. In general, the convergence rate of Ω -ERG energies towards FCI values depends on m and M , thus, the notation Ω -ERG(m,M) is used. It is found that the Ω -ERG(m,M) method can be very effective for calculating lowest-energy m (ground and excited) target states when a sufficiently large number of sweeps is used. We find that the fastest convergence is observed when $M > m$. The performance of the Ω -ERG(m,M) procedure in describing strongly correlated molecular systems has been illustrated by examining bond-breaking processes in N_2 , H_8 , H_2O and C_2 . The present, proof-of-principle study yields encouraging results for calculating multiple electronic states on potential energy surfaces with near Full CI quality.

Keywords: Ab initio Quantum Chemistry; Electronic Structure; Configuration Interaction; Potential Energy Surfaces; Excited States.

1. Introduction.

The development of efficient and reliable many-body approaches focusing on a problem of electron correlation is of great importance in physics and chemistry [1-4]. Density functional theory (DFT) has demonstrated remarkable success [5] in describing equilibrium geometries (local minima on potential energy surfaces) and associated properties of many diverse molecular systems, e.g. organometallic molecules [6] as well as organic magnets [7-9]. One of the major challenges for *ab initio* methods is calculation of potential energy surfaces for ground and excited electronic states [10]. Despite significant progress much work still needs to be done in this area. There are two considerations when pursuing the development of electron correlation theories, one focuses on strong (or static) correlation, and another on weak (or dynamic) electron correlation (see e.g. ref. [11]). While the first step focuses on zeroth-order wave functions capable of describing strong correlations, the improvement of such wave functions to describe dynamical electron correlation is essential if high-accuracy in molecular properties is required. For instance, a typical case requiring the inclusion of dynamical correlation is calculation of potential energy surfaces capable of yielding near-spectroscopic accuracy in computed rotational-vibrational energy levels [12-23]. The description of strong correlations relies on a properly chosen zeroth-order wave function. Such wave function can serve as a good reference function to include finer correlation effects associated with dynamical correlation in a systematic way. Most frequently, when highly correlated wave functions are sought, a reference function consists of a small expansion of most important Slater determinants. The reference function is usually defined in terms of strongly-occupied molecular orbitals referred to as Fully Optimized Reaction Space (FORS) [24,25] or Complete Active Space (CAS) [26]. The selection of active space in multi-configurational wave functions is a very important topic and has been recently discussed in literature (see, e.g. refs. [27,28]). The Full Configuration Interaction (FCI) approach [1,2,29] yields the exact solution (for a given basis set) and addresses both static and dynamic correlation problems, simultaneously. A considerable effort has been focused to develop computationally efficient algorithms for obtaining FCI quality wave functions and energies (see, e. g. refs. [2,4,30-34]). Since FCI approach is associated with exponential computational scaling, much research has been focused on the development of less computationally demanding *ab initio* methods for strongly correlated molecular systems. Examples of such methods include:

truncated (limited) CI methods [35-62] and CI methods with various extrapolations [63-74], multireference coupled cluster (CC) methods [75-80], iterative variational approaches [81-86], various methods based on density-matrices [87-90], matrix product states (MPS) and tensor product states (TPS)-based approaches [91-95] which include popular density-matrix renormalization group (DMRG) method [96-109], tree tensor networks [110], nonlinear wave functions [111-116], various hybrid methods combining coupled-cluster and MPS [117], different versions of CC that capture strong correlation [118-121], Spin-Flip approaches [122,123], methods based on symmetry breaking and restoration [124-126], methods based on Valence Bond-approaches [127], Quantum Monte Carlo approaches [128-131] and many others. In addition, we note that quantum information theory has been found useful in providing conceptual understanding of bond-forming and bond-breaking processes [132].

The concept of seniority, recently borrowed from nuclear physics [133-135], is expressed in terms of the quantum number Ω [53]. It has been found very useful in earlier investigations [53,54,136-140] in providing a compact description of electron correlation. In our earlier studies [53,54], the seniority number Ω was used to explore novel CI-selection schemes where criteria for excluding configurations in truncated CI-expansions are determined using criteria based on Ω . Such Ω -truncated CI-expansions along with orbital-optimization procedure have been shown [53,54] to offer a promising avenue for efficiently describing electron correlation in strong correlation regime, e.g. in molecular dissociations. In this study, however, we use the seniority number Ω to order Slater determinants in Full CI expansion (without truncation) for the use in a renormalization group (RG) procedure. Thus, in the RG procedure all configurations from the Full CI expansion are effectively considered. In particular, here we use Ω in the context of the energy renormalization group (ERG) approach of Wilson [141,142]. We note that the energy renormalization group (also called numerical renormalization group) methodology is focused on obtaining the lowest-energy states of *ab initio* Hamiltonians (see, e.g. refs. [105,143,144]). Thus, the present approach is called the Ω -ERG method. In this proof of principle investigation it is shown that the Ω -ERG method is capable of representing N-electron wave functions for *ab initio* quantum chemical Hamiltonian in a compact way. The performance of the Ω -ERG procedure in describing strongly correlated molecular systems has been illuminated by examining bond-breaking processes in N_2 , H_8 , H_2O and C_2 . We note that while iterative approaches for describing electron correlation have been already discussed in literature (see e.g. refs. [81-86]), in most

cases, the main focus is on the ground electronic state of *ab initio* Hamiltonian. For instance, the study in ref. [86] explored ground state of H₂O at several stretched geometries and discussed extensions for describing the *first two states* at equilibrium geometry of the H₂O molecule. In other studies, iterative CI-methods have been applied for describing many low-lying states of quantum systems using simplified (not *ab initio* quantum mechanical) Hamiltonian, like in the case of jellium model for Na₈ metal cluster at fixed equilibrium geometry [85]. For a nice overview of existing iterative approaches the reader is referred to ref. [86]. The Ω -ERG method presented in this work is based on the energy renormalization group approach and seniority number concept and is capable of describing *many* low-lying states of *ab initio* quantum chemical Hamiltonian along non-equilibrium geometries yielding FCI-quality results for a given basis set. In this context, we would like to mention that a different-type of RG approach, namely the density-matrix-renormalization-group (DMRG) method pioneered by White [96] has been also very successful for describing strong correlation of ground electronic states. However, in DMRG the criterion for the iterative truncation procedure is based on the reduced density matrix rather than in energy [96-110].

II. COMPUTATIONAL DETAILS.

Calculations for N₂ (STO-3G basis set), H₈ (STO-3G basis set) and H₂O (3-21G and 6-31G basis sets) and C₂ (6-31G basis sets) have been performed along symmetric dissociation paths. RHF, MCSCF and FCI computations have been carried out by one of us (LB) using the GAMESS quantum chemistry package [145]. The Ω -ERG(m, M) computations have been carried out by one of us (LB) using in-house pilot code with integral files generated by GAMESS programs [145].

III. The Ω -ERG method

The Ω -ERG procedure uses Slater determinants of the Full CI expansion that are ordered in a *systematic way* where more important determinants (i.e. determinants that have larger weight in a wave function) are included in the Ω -ERG procedure before determinants that are less important

(i.e. determinants that have lower weight in a wave function). It is possible to estimate the weight of a determinant or configuration *a priori* and generate CI expansions where Slater determinants are sorted based on a specific procedure [43] while making use of low-substitution-level determinants and exploring the sparsity [41,42] of the FCI wave function. Other methods that are similar in this context can also be found in literature [2,35-37]. Recently, Evangelista and co-workers introduced a method called adaptive configuration interaction (ACI) approach [48,49] for constructing simple multiconfigurational wave functions specified uniquely by an energy cutoff. However, in the present study we use a straightforward and systematic way to order determinants according to their seniority number Ω . This choice is based on our previous findings [53,54] indicating that a balanced description of potential energy surfaces (PES) can be achieved when determinants corresponding to lowest- Ω values are considered first, and a gradual improvement of such wave functions is achieved when configurations corresponding to higher Ω values are added in a consecutive way. Furthermore, *within* each seniority sector, the order of construction of configurations also depends on a list of *ordered* molecular orbitals. In this study we use Hartree-Fock orbitals that are ordered according to their orbitals energies or natural orbital [146] occupation numbers unless explicitly stated otherwise. However, in general, other choices of MOs can also be utilized, e.g. split-localized MOs [42] or QUAMBOs [147,148]. Finally, within each seniority sector the order in which determinants are generated depends on exact algorithm of construction. Thus, the proposed Ω -ERG method uses Slater determinants that are *ordered* according to seniority number Ω in ascending order. In the Ω -ERG procedure, *the active system* consists of M (N -electron) states and K additional complement (N -electron) states (*complement-system*). Among M states in the active system, the lowest-energy m states represent target states of interest (*target-states*), thus $m \leq M$. On the other hand, *the environment* consists of Full Configuration Interaction (CI) determinants that represent a reservoir from which the complement-states K are being selected. The goal of the Ω -ERG procedure is to obtain lowest-energy target states m of FCI-quality at a reduced computational cost in an iterative fashion. In general, the convergence rate of the Ω -ERG procedure towards the FCI result depends on m and M , thus, the notation Ω -ERG(m,M) is used. At each iteration, the resulting (small) Hamiltonian matrix of dimension $(M+K) \times (M+K)$ is diagonalized and only M lowest-energy roots (states) are kept for next iteration when K' determinants are added from the environment list to form a new

Hamiltonian matrix of dimension $(M+K') \times (M+K')$. In general, the numerical value of K depends on the value of seniority-number Ω of determinants that are being added and therefore, it will depend on the specific iteration. A higher seniority number Ω implies that a larger number of α/β electron-spin couplings need to be considered for a given set of singly-occupied MOs. Note that in all cases considered in this study the number of α -spin electrons is equal to the number of β -spin electrons. A *sweep* is completed after all determinants from the Environment (Full CI expansion) had been used in the Ω -ERG procedure. After the first sweep is complete, the Ω -ERG(m,M) procedure is repeated using M lowest-energy states from sweep-one and adding additional K determinants from the Environment. The iterative process is repeated with increasing number of sweeps until satisfactory convergence in energy for all m -target states is achieved. It is found that the Ω -ERG(m,M) method can be very effective for calculating the lowest-energy m target (ground and excited) states approaching Full CI result as the number of sweeps increases, meaning that the method is numerically exact. In this study we focus on molecular orbital ordering, number of target states m and number of lowest energy states kept after each diagonalization (M) in order to explore how these factors affect rates of convergence towards exact N -electron eigenstates of quantum mechanical Hamiltonian. The performance of the Ω -ERG(m,M) procedure in describing strongly correlated molecular systems is illustrated by examining bond-breaking process in N_2 , H_8 , H_2O and C_2 (See **Table 1** for information regarding CI wave functions for these systems). The spatial symmetry representing a totally-symmetric irreducible representation of a point group corresponding to a molecular geometry is maintained for all wave functions considered in this study.

A. Definitions relevant to the Ω -ERG(m,M) procedure

Here we introduce the relevant definitions:

(A) *Active System*: a set of M determinants (states) that will be included in the construction of the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$. Note that lowest energy M -states will be kept after each iteration of the Ω -ERG(m,M) procedure for use in next iteration.

(B) *Complement System*: a set of K determinants (see **Table 1** for K value for each Ω -sector) from *the Environment* (see below), which in addition to the M determinants form *the Active System* that will be used in the construction of the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$. Thus, at each iteration the Hamiltonian matrix has a dimension of $(M+K) \times (M+K)$. We note that the K -values in the Ω -ERG(m,M) implementation used in this study are linked to the magnitude of the seniority number Ω as shown in **Table 1**. However, the parameter K can be fixed at a relatively small value for all Ω -sectors if desired. For instance, for larger systems and seniorities it will be necessary to partition parameter K to keep dimensions of matrices that are diagonalized in the ERG procedure small.

(C) *Environment*: a reservoir from which determinants are selected and added to the *Complement System* (see above) in each iteration. In this study, except for the first-sweep, the Environment contains a complete set of Full CI determinants. In the first sweep, the first M determinants (in the $\Omega=0$ sector) from the FCI list are chosen to represent *Active System*. Note that after each iteration new determinants, i.e. determinants that have *not* been used in the formation of the Hamiltonian matrix in current sweep are selected from the Environment to be added to the Complement System.

(D) *Target states*: a set of lowest-energy m solutions ($m \leq M$) that are sought in the Ω -ERG(m,M) procedure.

B. The Energy Renormalization Group Ω -ERG(m,M) procedure

Step-1) Formation of ordered set of Full CI determinants. The determinants are ordered according to Ω -sectors in ascending order, namely $\Omega = 0, 2, 4, 6, \dots$ and so on.

For a list of ordered determinants within each Ω -sector see an illustration of N_2 (STO-3G basis set) in the Supplementary material.

See **Table 2** for the ordering of determinants in the $\Omega=0$ case (N_2 , STO-3G basis set).

Step-2) Formation of the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$ for the first iteration of the Ω -ERG(m,M) procedure.

Construct the Hamiltonian matrix of the dimension of $(M+K)\times(M+K)$ using $K+M$ ordered CI-determinants. Note that K value depends on Ω (see **Table I**).

Step-3) *First iteration:* Diagonalization of the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$ of dimension $(M+K)\times(M+K)$.

After the diagonalization is complete, the M lowest-energy roots are kept, while K highest-energy roots are omitted from further consideration.

Step-4) Formation of new Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$ for the next iteration of the Ω -ERG(m,M) procedure.

Construct the Hamiltonian matrix of the reduced $(M+K)\times(M+K)$ dimensions using M states kept from the previous iteration and adding K new CI-determinants from the Environment (these K determinants represent the new Complement System).

Step-5) Repeat Steps 2 to 4 until the full list of Full CI determinants from the Environment is exhausted.

This completes the first Ω -ERG(m,M) sweep.

Step-6) Now, consider only M lowest energy states resulting from the first Ω -ERG(m,M) sweep representing a new Active System. Add K determinants from the ordered set of Full CI list of determinants in the Environment.

(Note that these are *the same* determinants used in the first sweep).

Since the M states and these K determinants are not linearly independent, orthonormalize the set of $(M + K)$ states which requires formation and diagonalization of the overlap matrix $\mathbf{S}(\mathbf{i},\mathbf{j})$.

Any states that have zero-eigenvalue of the overlap matrix are removed.

We use the *canonical* orthonormalization procedure [1]. After the set of orthonormal states is determined, construct the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$.

Step-7) *Next iteration:* Diagonalize of the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$.

After the diagonalization is complete, the M lowest-energy roots are kept, while highest-energy roots are omitted from further consideration.

Step-8) Keep M lowest energy states (eigenvectors), and add K' new determinants from the Environment (these K' determinants represent the Complement System).

Then, construct the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$ and Overlap matrix $\mathbf{S}(\mathbf{i},\mathbf{j})$ of $(N+K') \times (N+K')$ dimensions using these $N+K'$ vectors.

Note that K' value depends on Ω value (see **Table 1**).

Orthonormalize the set of $M + K'$ states which requires diagonalization of the overlap matrix $\mathbf{S}(\mathbf{i},\mathbf{j})$. Any states that have zero-eigenvalue of the overlap matrix are removed to ensure linearly-independent set of N -electron states. After the set of orthonormal states is determined, the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$ is formed.

Step-9) *Next iteration:* Diagonalize the Hamiltonian matrix $\mathbf{H}(\mathbf{i},\mathbf{j})$.

After the diagonalization is complete, the M lowest-energy roots are kept, while highest-energy roots (beyond M) are omitted from further consideration.

Step-10) Repeat Steps 8 and 9 until the complete list of Full CI determinants is exhausted.

This completes the latest Ω -ERG(m,M) sweep.

Step-11) Repeat Steps 6 to 10 until energies of the m target states do not change within the given tolerance of ε . *This completes the Ω -ERG(m,M) procedure.*

We shall use symbol δ to represent the deviation of ERG-values from the exact, i.e. FCI-benchmark. A comment regarding the K -value shown in **Table 1** used in forming the Complement System of K determinants in each iteration of the Ω -ERG(m,M) procedure is appropriate at this point. The calculation of K value for each Ω is based on the combinatorial formula:

$$K = \frac{(MOS)!}{(N_\alpha)! \times (N_\beta)!} \quad (1)$$

Where the symbol (MOS) represents a number of singly-occupied molecular orbitals in a set of occupied MOs, N_α is the number of singly-occupied-MOs occupied by electrons having α -spin and N_β is the number of singly-occupied-MOs occupied by electrons having β -spin. For example, if **A** and **B** are singly-occupied MOs then there will be two possibilities for α and β electron-pair: $\{\mathbf{A}(\alpha), \mathbf{B}(\beta)\}$ and $\{\mathbf{A}(\beta), \mathbf{B}(\alpha)\}$, thus $K=2$. An example displaying the full list of determinants and α - and β -strings associated with them is provided in the Supplementary material for the case of N_2 . One can expect that the selection of K value as given by Equation (1) should facilitate the convergence of the Ω -ERG(m, M) procedure. Again, as mentioned above, the parameter K can be fixed at a constant and relatively small value for all Ω -sectors if desired. Since the numbers of α - and β -electrons are the same in all cases considered in the present study, one has $M_s = 0$ for all wave functions. The Ω -ERG(m, M) procedure yields $M_s=0$ components of pure spin states (singlets, triplets, quintuplets,...etc). In addition, the spatial symmetry representing totally-symmetric irreducible representations of point groups representing molecular geometries is maintained for all wave functions.

A few comments are appropriate at this point. After the first sweep of the Ω -ERG(m, M) procedure, the lowest M states are generated as specific linear combinations of determinants. While after the initial sweep these M states may not be optimal, in following sweeps as additional determinants are included, these lowest states are gradually improved producing new M states that are represented by more optimal linear combinations of determinants. Due to flexibility of the iterative procedure when *all* determinants of FCI expansion are considered in compact way, the Ω -ERG(m, M) procedure is expected to ultimately converge to M exact benchmark (i.e. FCI) energy values. The exceptions can happen when, at early-sweep-stage, among the lowest $m=M$ roots, there is a root (we shall call it root-X) that is an *exact* solution to a *higher-energy* FCI state. In other words, root-X happens to be the L -th root of FCI solution, where $L > M = m$. If such a situation occurs, then the Ω -ERG(m, M) procedure may not be able to “switch” high-energy root-X with a lower-energy state, simply by increasing the number of ERG sweeps. The remedy to the situation when a high-energy root gets “stuck” in the small space of $m=M$ roots is to increase the value of M while keeping m unchanged, thus having $m <$

M. By starting a new Ω -ERG(m, M') procedure where $M' > m$, one will observe that the root- X of the earlier Ω -ERG(m, M) procedure with $m=M$ which (incorrectly) occurred as m -th root will be replaced by the correct, i.e. m -th root of the FCI solution. We shall examine such a situation when discussing the symmetric dissociation of H_8 later in this study which illustrates limitations of the ERG procedure.

One may also ask: If all FCI determinants are considered in the Ω -ERG(m, M) procedure, why ordering of determinants (in terms of ascending seniority numbers) gradually added to the space of M lowest ERG-roots matter at all? The answer to this question has to do with the rate of convergence to the exact FCI benchmarks. Since earlier studies [53,54] indicated that low-seniority sectors provide reliable and balanced description of bond-breaking chemical processes, it is reasonable to surmise that it is helpful to order the determinants in such a way that more-important determinants would be considered *before* determinants that are less important contributors to lowest energy states. In addition, it is important to note that in the ERG-procedure one starts with a very small number, namely M of N -electron states (determinants), that are improved at *each iteration* by adding K determinants from the Environment and after diagonalization of the Hamiltonian matrix of dimensions $M+K$ by $M+K$, the new, lowest M roots become linear combinations of determinants, and so on. Thus, the quality of the starting M states (determinants) is important for the fastest convergence toward exact lowest-energy FCI-quality states in this iterative procedure.

Finally, a comment needs to be made regarding the size of basis set and, as a consequence the length of FCI expansions considered in this work. As it was mentioned earlier, we intentionally chose relatively small basis sets and FCI expansions, to reduce the cost and time of our ERG calculations. One may wonder if our principal conclusions about the essence of ERG method and its convergence patterns will be less favorable when larger basis sets and FCI expansions are considered. Firstly, one can say that, ultimately, the size of CI Hamiltonian matrix is a more significant factor than the number of iterations. Secondly, to explore the effects of basis set size and/or the FCI expansion size on the rates of convergence of our ERG method, we consider four molecular systems where the size of FCI expansion increases roughly by a factor of 10, namely, 396, 2468, 61441, and 414864. We note that our pilot-code implementation of the ERG procedure is not as efficient as it can be made to be. Also, it is true that actual timings of our ERG procedure to reach exact FCI benchmarks are higher compared

even to a straightforward application of FCI codes available in standard *ab initio* quantum chemistry packages. However, our primary goal in this study is to explore the validity of the ERG procedure to find out *if* and with *how many sweeps* it converges to benchmark/exact FCI solutions for various selections of parameter m and M values. At the current stage of our pilot-code, it is practical to treat M values up to 50, and K values up to 70.

IV. Applications of the Ω -ERG(m,M) method

A. N_2 potential energy curve

A challenging case that illustrates a strong correlation problem is dissociation of the N_2 molecule which has been used extensively to estimate the performance of new *ab initio* methods [53,54,97,48,49,138,149-151]. For simplicity, we choose STO-3G basis set. The spatial symmetry of the wave function corresponds to the A_g irreducible representation of D_{2h} point group. Core 1s-electrons are kept doubly-occupied at all times. The valence-electron correlated active space is (10 electrons in 8 orbitals) for Full CI wave function which contains 396 Slater-determinants. The CI determinants are ordered according to Seniority (Ω) sectors ($\Omega=0, 2, 4, 6$) in ascending order (see **Table 1**). In particular, $\Omega = 0$ sector has 56 determinants, $\Omega = (0+2)$ sectors contain 116 CI determinants, $\Omega = (0+2+4)$ sectors contain 356 CI determinants, and $\Omega = (0+2+4+6)$ sectors contain 396 CI determinants. See **Table 2** for ordering of determinants for $\Omega=0$ case.

In exploring the N_2 dissociation case, we will focus on: molecular orbital ordering, number of target states m and the number of the lowest energy states kept after each diagonalization (M) in order to examine how these factors affect the rate of convergence towards exact N -electron eigenstates of the quantum mechanical Hamiltonian. The number of added K new N -electron states (Slater determinants) to the previously determined (and kept) states M depends on Ω (see **Table 1**). We use Restricted-Hartree-Fock (RHF) molecular orbitals ordered according to their *orbital energies* unless explicitly noted otherwise. The list of the FCI determinants has been ordered according to their Ω (from 0 to 6). **Table 2** illustrates the order of determinants for $\Omega=0$. For the ordering of determinants for $\Omega=0$, $\Omega=2$, $\Omega=4$ and $\Omega=6$ cases, the reader is referred to the Supplementary material. Our target in the case of N_2 is *four* lowest-

energy states (i.e., $m=4$) at various internuclear distances. **Figure 1** displays graphically these potential energy curves for N_2 .

First, we focus on the performance of the Ω -ERG(m,M) procedure in converging to the exact energy only for the *lowest-energy root*, i.e. *ground-state (GS)* with $m=1$ at three internuclear distances, $R=1.2$ Å (near-equilibrium distance for the GS), $R=1.6$ Å and $R=2.4$ Å. We choose $M = 4$ (four *lowest-energy states kept* after each iteration). The performance of the Ω -ERG(m,M) procedure is illustrated in **Figure 2** ($m=1$ and $M=4$) where we plot logarithmic energy error in Hartree (h) versus the number of ERG sweeps. **Figure 2** clearly demonstrates that the convergence of the ground-state energy towards its exact value is very rapid for at 1.2 Å and it becomes slightly slower as the internuclear distance increases. For orbital specifications the reader is referred to the Supplementary material. From the data listing natural-orbital (NO) occupation numbers (see the Supplementary material), one can see that while at $R=1.2$ Å NO-occupation numbers are close either to 2 or 0, by contrast, at $R=2.4$ Å there are four NO-values that are close to 1, one NO-occupation number of 1.3 and one NO-occupation of 0.7 while other NOs are doubly-occupied indicating a near-dissociation limit approaching separate (N + N) atomic states.

Next, we examine $m = 4$ lowest states at 1.2 Å, 1.6 Å and 2.4 Å using the Ω -ERG(m,M) procedure with two M choices: $M = 4$ and $M = 8$ (see Supplementary material for data corresponding to cases $R=1.2$ Å and $R=1.6$ Å). The most challenging cases for the convergence rate of Ω -ERG(m,M) method occur when $m=M$. For example, for $R=1.6$ Å case, the ERG energies converge to exact values within $\delta=10^{-10}$ Hartree as follows: for the Ω -ERG($m=2,M=2$) procedure after 14 sweeps for $m=2$ roots, for the Ω -ERG($m=3,M=3$) procedure after 12 sweeps for $m=3$ roots, for the Ω -ERG($m=4,M=4$) procedure after 24 sweeps for $m=4$ roots, and for the Ω -ERG($m=5,M=5$) procedure after 32 sweeps for $m=5$ roots. Even in the $R=2.4$ Å case, the Ω -ERG($m=5,M=5$) procedure yields all lowest $m=5$ roots within $\delta=10^{-10}$ Hartree from exact results after 50 sweeps (see the Supplementary material). The convergence at 1.2 Å (near-equilibrium bond-length) is very rapid for the lowest-energy $m=4$ target states even for the least favorable, $m = M = 4$ case. The lowest three roots converge within $\delta < 4 \times 10^{-10}$ Hartree from their FCI benchmarks after only 6 sweeps. For the highest (fourth) root the deviation at sweep=6 is still about $\delta \cong 2.0 \times 10^{-5}$ h, and it reduces to about $\delta \cong 1 \times 10^{-10}$ h at sweep = 16. On the other hand,

if $M = 8$, all four lowest roots converge within $\delta \leq 4.0 \times 10^{-10}$ h from FCI benchmarks only after 9 sweeps. For the case $R=2.4$ Å (see **Tables 3** and **4**) the convergence of the lowest four roots requires more sweeps to achieve the same accuracy compared to cases $R=1.2$ Å and $R=1.6$ Å due to the fact that one has to deal with a higher-degree of bond-length stretch. For example, This already can be seen in the comparison of two simplest cases, Ω -ERG($m=2, M=2$) and Ω -ERG($m=2, M=3$). The graphical display in **Figure 3** demonstrates that the convergence towards two lowest states is much faster for $M=3$ case. The Ω -ERG($m=4, M=4$) procedure focuses on four lowest states and the convergence data is listed in **Table 3**. While after 18 sweeps the Ω -ERG($m=4, M=4$) procedure yields the lowest two roots within $\delta = 2.0 \times 10^{-10}$ h, the third and fourth roots have deviations of 1.1×10^{-4} h and 2.6×10^{-3} h, respectively (see **Table 3**). However, as shown in **Table 4**, increasing M from 4 to 8 allows to improve the convergence considerably, and in the Ω -ERG($m=4, M=8$) procedure *all four* lowest roots converge to within $\delta = 1.3 \times 10^{-9}$ h only after 24 sweeps. Thus, the data above clearly demonstrate that having ($m < M$) accelerates the Ω -ERG(m, M) convergence of m lowest roots to its exact benchmark values of FCI calculation, especially at large internuclear distances. More information about the convergence patterns of the Ω -ERG(m, M) method can be found in the Supplementary material.

Overall, the performance of the Ω -ERG(m, M) method at various stretched geometries along the N_2 dissociation pathway demonstrate that the order of molecular orbitals can affect the ERG convergence rate for $m=M$ cases. However, when $m < M$, the ERG convergence is much less sensitive to MO ordering. Thus, it is advantageous to choose $m < M$ if the most robust and fastest convergence is sought.

B. H_8 potential energy curve

Symmetric dissociation of hydrogen-chains and hydrogen-cubes have been used extensively to test theoretical methods aimed at describing strong correlation [53,138,152-156]. In ref. [53] the symmetric dissociation of the H_8 chain in its ground-electronic state was used to explore the usefulness of seniority number in establishing a FCI hierarchy. The study in ref. [53] demonstrated that criterion for truncating CI expansion based on the seniority number Ω offers a good alternative to electron-substitution-level based truncation schemes in strong correlation

case. Here, we revisit the symmetric dissociation of the H_8 chain and explore performance of the Ω -ERG(m,M) scheme in converging lowest m roots/states at various internuclear distances along symmetric-dissociation curves. We focus on A_g spatial symmetry states (irreducible representations) of the D_{2h} -point group. **Figure 4** displays *seven* lowest potential energy curves calculated at FCI level of theory using RHF orbitals ordered according to their energies. From **Figure 4** it can be seen that $R_e = 0.95 \text{ \AA}$ represents an equilibrium bond-length for equidistant H-H internuclear separations between adjacent H-atoms in the H_8 chain. Thus, in order to explore the strong correlation regime, we focus on internuclear distances that are much larger than R_e . First, we focus on the lowest four roots/states ($m = 4$) calculated at significantly distorted bond-length distance of $R = 1.8 \text{ \AA}$. In the Ω -ERG(m,M) procedure, we order all RHF orbitals according to their energies, and construct Slater determinants ordering them according to their seniority number in ascending fashion ($\Omega = 0, 2, 4, 6, 8$). There are 2468 Slater determinants of spatial symmetry A_g (see **Table 1**). For numerical data illustrating performance of the Ω -ERG(m,M) method at $R=1.0 \text{ \AA}$, $1.8 \text{ \AA}$ and $2.4 \text{ \AA}$ (see the Supplementary material).

The data for intermediate and large inter-nuclear and equidistant separations between neighboring hydrogen atoms along a potential energy curve for symmetric dissociation of the H_8 system are displayed graphically in **Figures 5** and **6**. **Figure 5** illustrates the convergence rate for the lowest $m=4$ states at $R=1.8 \text{ \AA}$ while **Figure 6** shows the convergence of $m=4$ states at $R = 2.4 \text{ \AA}$ as number of ERG sweeps increases. **Figure 5** displays total energies for the lowest four target states ($m=4$) with $M=6$ (left panel) and $M=20$ (right panel) selections for the ERG method. From **Figure 5** it is clear that the convergence for the lowest target states in the Ω -ERG($m=4,M=20$) procedure is considerably faster compared to the Ω -ERG($m=4,M=6$) method. For instance, for the case Ω -ERG($m=4,M=6$) at sweep = 15, the energy errors δ relative to FCI benchmark are: 0.010 mh, 0.031 mh, 0.253 mh and 1.048 mh for the first (ground-state) (1A_g), second (3A_g), third (1A_g), and fourth (3A_g) roots, respectively. By contrast, for the case Ω -ERG($m=4,M=20$) at sweep = 15, the energy errors δ relative to FCI-benchmark are: 0.000158 mh, 0.000878 mh, 0.000206 mh and 0.014935 mh for the first (ground-state), second, third and fourth lowest-roots, respectively. The procedure works also well if the number of target states is larger than 4. For instance, $m=8$ states converge within $\varepsilon=10^{-10}$ h tolerance in the Ω -

ERG($m=8, M=20$) procedure after 90 sweeps yielding eight lowest states for $R=1.8 \text{ \AA}$ case, each within $\delta=10^{-10} \text{ h}$ from benchmark result (see the Supplementary material).

A short comment regarding the question of convergence of the Ω -ERG(m, M) procedure for the least favorable case when $m=M$ is appropriate. At near-equilibrium geometry ($R=1.0 \text{ \AA}$), we observe that all target states converge with accuracy of $\delta = 10^{-10} \text{ h}$ for Ω -ERG($m=4, M=4$) and Ω -ERG($m=6, M=6$) after 65 sweeps yielding exact lowest states of the FCI calculation (see the Supplementary material). For stretched geometries, e.g. $R=1.8 \text{ \AA}$, the convergence of the Ω -ERG(m, M) procedure when $m=M$ is considerably slower (see **Table 5**). For the Ω -ERG($m=4, M=4$) procedure *all four roots* converge within $\varepsilon = 1 \times 10^{-10}$ Hartree at sweep = 150, but only the first *three roots* match exact benchmark values within $\delta = 1 \times 10^{-10} \text{ h}$. The highest (fourth) root from the Ω -ERG($m=4, M=4$) procedure has energy of -3.61280 Hartree which matches state-38 (9A_g) of the FCI calculation (see the Supplementary material). Evidently, the root-4 of the Ω -ERG($m=4, M=4$) procedure that represents high-spin-multiplicity state *does not* interact with any state of the environment and is fully contained in the subspace of $m=M=4$ states. The energy for the state-4 of the FCI solution is -3.78245 h (see **Table 5**). Also, the results in **Table 5** show that for cases Ω -ERG($m=6, M=6$) and Ω -ERG($m=8, M=8$) the highest root, i.e. root-6 and root-8, respectively, *does not* yield the highest state, i.e. state-6 and state-8 of FCI solution, correctly. Once again, the highest converged ERG root in Ω -ERG($m=6, M=6$) or in Ω -ERG($m=8, M=8$) procedure matches state-38(9A_g) of the FCI calculation. In order to obtain the lowest exact states of FCI-calculation correctly using the Ω -ERG(m, M) procedure, a larger M value (i.e. $m < M$) must be selected. As can be seen from **Table 5**, for the procedures Ω -ERG($m=4, M=6$), Ω -ERG($m=4, M=10$) and Ω -ERG($m=8, M=20$), all m lowest energy ERG-roots converge to correct m FCI-solutions, and the convergence is *faster* for larger M values.

Even more dramatic effect on the convergence rate of the lowest $m=4$ roots in the Ω -ERG(m, M) procedure due to the increase of M value is seen at internuclear distance of $2.4 \text{ \AA}$ where total energies of four lowest states are very close to the dissociation limit of eight separate hydrogen atoms (see the Supplementary material for details). The relevant data is displayed graphically in **Figure 6** for the following cases: Ω -ERG($m=4, M=8$) (left-panel), Ω -ERG($m=4, M=12$) (middle-panel) and Ω -ERG($m=4, M=20$) (right-panel). In particular, the increase of M value from 8 to 20, reduces the largest deviation observed for *state-4* from 1.51 mh

to only 0.20 mh if only 15 sweeps are considered. At sweep=310 of the Ω -ERG($m=4, M=20$) procedure the first three roots are converged within tolerance of $\varepsilon=1\times 10^{-10}$ h having deviations from benchmarks within $\delta=1\times 10^{-10}$ h. The *root-4* has converged within tolerance of $\varepsilon = 4\times 10^{-9}$ h with a deviation from benchmark within $\delta = 1\times 10^{-8}$ h (see the Supplementary material).

Overall, the data for the symmetric dissociation of the H_8 chain indicate that, in general, higher-energy roots require more sweeps to converge within a given accuracy ε than lower roots. Furthermore, the convergence rate of the Ω -ERG(m, M) method can be increased dramatically when option $m < M$ is chosen, which allows higher roots to converge smoothly to the corresponding exact lowest FCI-quality values without them getting stuck at a higher-energy FCI solution.

C. H_2O symmetric dissociation

The next example illustrating the performance of the Ω -ERG(m, M) method is the symmetric dissociation of the H_2O molecule which represents a challenging and useful case for testing new *ab initio* methods (see, e.g. refs. [54,150,151]). In the recent study [54] the symmetric dissociation of H_2O was considered to explore hybrid truncated-CI wave functions using seniority-number Ω and substitution/excitation level $EXC_{\max}$ with respect to a reference function. The experimentally-derived equilibrium geometry for the ground-state of H_2O is $R_e(OH) = 0.9572$ Å and $\text{angle}(HOH)=104.52^\circ$ (see, e.g. refs. [54,157]). In our calculations we keep the angle $(HOH)=104.52^\circ$ fixed and vary only the internuclear distance R_{OH} . Basis sets 3-21G and 6-31G are used in order to keep computational costs low. The FCI wave function contains 61441 Slater determinants for A_1 -symmetry states.

As in cases discussed above, we will primarily focus on stretched distances, e.g. $2R_e$ and $3R_e$ since wave functions to be computed by the Ω -ERG(m, M) procedure contain increasing amounts of static correlation with the increase of the bond length. We use molecular orbitals obtained from 2-state-averaged MCSCF calculations using Full Valence Space FVS[8,6] in order to treat energetics of ground and excited states in a more balanced way (see the Supplementary material for details). Two-states included in state-averaged calculations are 1A_1 (singlet) and 3A_1 (triplet). The list of the FCI determinants has been constructed using these MOs and determinants have been ordered according to Ω from 0 to 8 (see **Table 1**). The data

illustrating the rate of convergence of the Ω -ERG(m,M) energies for lowest six ($m=6$) states of A_1 symmetry calculated using 3-21G basis sets are displayed graphically in **Figure 7** in terms of logarithmic energy error (in hartree) versus the number of RG sweeps. Left and middle panels of **Figure 7** represent data at $2R_e$ for Ω -ERG($m=6,M=8$) and Ω -ERG($m=6,M=10$), respectively, while the right-panel corresponds to the internuclear distance $3R_e$ and Ω -ERG($m=6,M=16$) case. The data for $R=2R_e$ shows that the most significant acceleration in the ERG convergence is observed for the second lowest (triplet-state) going from $M=8$ to $M=10$. Most significantly, at $R=3R_e$, the Ω -ERG($m=6,M=16$) procedure has much faster convergence than for $M=8$ or $M=10$ at shorter distance of $2R_e$.

Potential energy curves describing the symmetric stretch in H_2O for lowest-energy states of A_1 -symmetry for 6-31G basis sets are displayed in **Figure 8**. We use the Ω -ERG(m,M) method to calculate total energies at internuclear distances R_e , $2R_e$ and $3R_e$ which are indicated by solid dots in **Figure 8**. In the Ω -ERG(m,M) procedure (6-31G basis set) we use molecular orbitals obtained from 2-state-averaged MCSCF calculations using Full Valence Space FVS[8,6] for A_1 as well. FCI determinants (61,441 Slater determinants) have been constructed using these MOs and determinants have been ordered according to their Ω in ascending order (see **Table 1**). Since the Ω -ERG($m=6,M=16$) for 3-21G basis set (see **Figure 7**) demonstrated rapid convergence, here, for 6-31G basis set we choose the Ω -ERG($m=6,M=16$) method to examine convergence for *lowest six states* in terms of logarithmic energy error (in hartree) compared to FCI energy benchmarks as the number of RG sweeps increases. The relevant data is displayed graphically in **Figure 9**. From left to right cases are: R_e (left-panel), $2R_e$ (middle-panel) and $3R_e$ (right-panel). In the R_e case one can see that the convergence is very rapid and that the energy error decreases fastest for lower-energy states and is somewhat slower for higher-energy states. For the $2R_e$ case, the Ω -ERG($m=6,M=16$) procedure displays a slightly slower convergence for the six lowest states compared to the R_e case. Finally, for the $3R_e$ case, the Ω -ERG($m=6,M=16$) method yields rapid and nearly identical rate of convergence for *all six* lowest-energy states indicating that *better than microHartree* accuracy (i.e. $\delta < 10^{-6}$ h) is achieved with only five RG sweeps which is very encouraging. For additional information regarding the convergence rates of the ERG procedures as well as converged energy values see the Supplementary material.

D. The C₂ case

The last example illustrating the performance of the Ω -ERG(m,M) method is the C₂ molecule. For the basis set 6-31G, the FCI wave function which correlates 8 valence electrons in 16 orbitals contains 414,864 Slater determinants of A_g-symmetry. For simplicity, we select the Ω -ERG($m=4,M=12$) procedure at R=1.2 Å inter-nuclear geometry which corresponds to near-equilibrium bond-length. For this selection of M value, the largest Hamiltonian matrix that is considered in the ERG procedure is 82×82. We compare the convergence rate of the Ω -ERG($m=4,M=12$) procedure in terms of numbers of ERG-sweeps with numbers of CI iterations of Full CI code (ALDET) of Ivanic and Ruedenberg [40] that is available in GAMESS Quantum Chemistry suite of programs [145]. For the Full CI code ALDET we choose several CI input specifications, namely, the size of initial CI guess matrix (ICIGM) and maximum number of CI expansion vectors. The relevant data are displayed in **Table 6** which lists only deviations from the benchmarks. For the total energy values the reader is referred to the Supplementary material. From **Table 6** one observes that the performance of the Ω -ERG($m=4,M=12$) procedure compares very well with the Full CI code (ALDET) for the size of initial CI guess matrix (ICIGM) of 300 when comparing sweep numbers with CI-iterations. Only when the size of initial CI guess matrix in the Full CI code is set to 3500, the number of CI iterations and the Ω -ERG($m=4,M=12$) sweeps at comparable stages yield similar deviations from benchmarks. While the standard (production-stage) Full CI code is significantly faster than the current pilot-implementation of the Ω -ERG procedure, the data shows that high-quality numerical results can be obtained using only very small CI matrices not exceeding 82×82 while Full CI expansion contains 414,864 Slater determinants. Also, in order to explore performance of the Ω -ERG procedure at *distorted geometries*, we examine the C₂ molecule at distorted inter-nuclear bond-length of 1.8 Å. The relevant data for Ω -ERG($m=3,M=10$) and Ω -ERG($m=3,M=14$) procedures are listed in **Table 7**. The data shows that the convergence rates of total energies with respect to the number of Ω -ERG sweeps at the inter-nuclear distance of 1.8 Å is slightly slower as compared to its performance at the equilibrium geometry of 1.2 Å. However, the convergence

rates for the lowest 3 states still exhibit rapid convergence (for more data, see the Supplementary Information).

Overall, the results presented in the C_2 case are very encouraging and can be useful when developing accurate *ab initio* methods that consider only very small Hamiltonian matrices.

V. Summary and Conclusions.

In the present study we have introduced the *energy (also called numerical) renormalization group* approach, Ω -ERG(m, M) for calculating Full CI energies of m lowest-energy electronic states. In the Ω -ERG(m, M) method, the ordering of Slater determinants is based on the seniority-number (Ω) in ascending order, i.e. determinants from lower- Ω sectors are included before higher- Ω sectors (i.e., $\Omega=0, 2, 4$, etc). For simplicity, we used small basis sets to test our pilot code of the Ω -ERG(m, M) procedure in order to keep the calculations tractable and to keep computational costs low. Also, we focused on small numbers of lowest target states m in most cases ($5 \leq m \leq 8$) to discuss the performance of the pilot-code of the Ω -ERG(m, M) procedure for dissociation of N_2 and H_8 and the water molecule. In addition, we calculated lowest states for the C_2 molecule at several inter-nuclear distances to see how the increase of the total number of determinants to be included affects the convergence rates in terms of ERG-sweeps. Our investigation shows that for the fastest convergence of the Ω -ERG(m, M) method it is beneficial to use M values that are larger than the number of target states m , i.e. $M > m$. However, even for the least favorable case of $m=M$ our ERG procedure is able to recover the exact m lowest-energy target eigenvalues with enough number of sweeps for most cases. The only exception occurred when the space of M lowest-states contained a high-spin (multiplicity = 9) state that did not interact with environment states when the selection $m=M$ was made. However, the increase of the M value in the Ω -ERG-procedure enabled the convergence of the all lowest m roots (target-states) toward correct FCI benchmarks.

The present investigation demonstrates that the Ω -ERG(m, M) method is capable of recovering Full CI energies within a chosen accuracy ε , for arbitrarily selected lowest energy states m representing various spin-multiplicities (singlets, triplets, quintuplets, etc.) along potential energy surfaces. One criterion that is relevant when discussing the computational cost

of the Ω -ERG(m,M) method is the dimension of largest matrix that needs to be diagonalized in the iterative ERG procedure relative to the size of Full CI expansion in terms of Slater determinants. The largest matrices diagonalized in the Ω -ERG(m,M) procedure have dimensions of 28×28 , 90×90 , 86×86 and 84×84 compared to FCI matrix-dimensions of 396×396 , 2468×2468 , 61441×61441 , and 414864×414864 for N_2 , H_8 , H_2O and C_2 , respectively. The rate of convergence of the ERG procedure towards benchmark values for lowest energy states is very similar for all these systems indicating that there is *no significant deterioration* of ERG convergence rates with RG-sweeps while the size of FCI expansion increases dramatically. A further improvement in the performance in the Ω -ERG(m,M) method can be achieved by incorporating protocols and concepts of quantum information theory as described in refs. [100-102,132].

Overall, the present proof-of-principle study indicates that the Ω -ERG(m,M) method for determining low-lying states (ground-state and excited states) along the dissociation paths is an effective and promising approach. There are many ways to improve the effectiveness of the iterative Ω -ERG(m,M) method, for example, one way is to select only the most important determinants in the trial expansion. In future applications, the Ω -ERG(m,M) method will be tested for other cases of strongly-correlated systems exploring truncated CI-expansions to explore its performance. For instance, the ERG-method can be useful within the context of the CEEIS-FCI method (see refs. [66-70]).

Supplementary material:

This Supplementary material lists raw data for describing the performance of the Ω -ERG method for N_2 , H_8 , H_2O and C_2 systems.

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Table 1. Seniority number (Ω) sectors in terms of numbers of Slater determinants in wave functions considered in the present study.

Ω -sectors	Number of Slater Determinants	K -value ^{a)}	Maximum Matrix-Dimension
I. N₂: 2-core-orbitals, Full-Valence-Space = (10 electrons in 8 orbitals), A_g-symmetry			
$\Omega=0$	56	1	
$\Omega=2$	60	2	
$\Omega=4$	240	6	
$\Omega=6$	40	20	
$\Omega=0,2,4,6$	396		
FCI			396×396
Ω-ERG(m,M)			28×28 ^{b)}
II. H₈: Full-Valence-Space = (8 electrons in 8 orbitals), A_g-symmetry			
$\Omega=0$	70	1	
$\Omega=2$	480	2	
$\Omega=4$	1368	6	
$\Omega=6$	480	20	
$\Omega=8$	70	70	
$\Omega=0,2,4,6,8$	2468		
FCI			2468×2468
Ω-ERG(m,M)			90×90 ^{b)}
III. H₂O: 1-core-orbital, Full-Valence-Space = (8 electrons in 12 orbitals), A₁-symmetry			
$\Omega=0$	495	1	
$\Omega=2$	5280	2	
$\Omega=4$	21336	6	
$\Omega=6$	25440	20	
$\Omega=8$	8890	70	
$\Omega=0,2,4,6,8$	61441		
FCI matrix:			61441×61441
Ω-ERG(m,M)			86×86 ^{b)}

^{a)} The K -value used in the Ω -ERG(m,M) procedure (see text) for each Ω -sector.

^{b)} Largest matrix diagonalized in the Ω -ERG(m,M) procedure.

Table 1 (continue). Seniority number (Ω) sectors in terms of numbers of Slater determinants in wave functions considered in the present study.

Ω -sectors	Number of Slater Determinants	K -value ^{a)}	Maximum Matrix-Dimension
IV. C₂: 2-core-orbitals, Full-Valence-Space = (8 electrons in 16 orbitals), A_{1g}-symmetry			
$\Omega=0$	1,820	1	
$\Omega=2$	11,648	2	
$\Omega=4$	93,456	6	
$\Omega=6$	188,800	20	
$\Omega=8$	119,140	70	
$\Omega=0,2,4,6,8$	414,864		
FCI			414864×414864
Ω-ERG(m,M)			84×84 ^{b)}

^{a)} The K -value used in the Ω -ERG(m,M) procedure (see text) for each Ω -sector.

^{b)} Largest matrix diagonalized in the Ω -ERG(m,M) procedure.

Table 2. N₂ (STO-3G basis set). The ordering of the determinants in terms of their electron occupations in valence molecular orbitals for $\Omega=0$ sector (56 determinants). For Full valence space, FCI = CAS[10,8]. Core (1s) orbitals on Nitrogen atoms are kept doubly occupied and are not shown.

No	Molecular Orbital electron occupations ^{a)}							
	A _g	B _{1u}	A _g	B _{3u}	B _{2u}	B _{3g}	B _{2g}	B _{1u}
1	2	2	2	2	2	-	-	-
2	2	2	2	2	-	2	-	-
3	2	2	2	2	-	-	2	-
4	2	2	2	2	-	-	-	2
5	2	2	2	-	2	2	-	-
6	2	2	2	-	2	-	2	-
7	2	2	2	-	2	-	-	2
8	2	2	2	-	-	2	2	-
9	2	2	2	-	-	2	-	2
10	2	2	2	-	-	-	2	2
11	2	2	-	2	2	2	-	-
12	2	2	-	2	2	-	2	-
13	2	2	-	2	2	-	-	2
14	2	2	-	2	-	2	2	-
15	2	2	-	2	-	2	-	2
16	2	2	-	2	-	-	2	2
17	2	2	-	-	2	2	2	-
18	2	2	-	-	2	2	-	2
19	2	2	-	-	2	-	2	2
20	2	2	-	-	-	2	2	2
21	2	-	2	2	2	2	-	-
22	2	-	2	2	2	-	2	-
23	2	-	2	2	2	-	-	2
24	2	-	2	2	-	2	2	-
25	2	-	2	2	-	2	-	2
26	2	-	2	2	-	-	2	2
27	2	-	2	-	2	2	2	-
28	2	-	2	-	2	2	-	2
29	2	-	2	-	2	-	2	2

^{a)} Molecular Orbital Symmetry-labels of D_{2h} point group (irreducible representation labels) are listed below.

Table 2 (continue). N₂ (STO-3G basis set). The ordering of the determinants in terms of their electron occupations in valence molecular orbitals for $\Omega=0$ sector (56 determinants). For Full valence space, FCI = CAS[10,8]. Core (1s) orbitals on Nitrogen atoms are kept doubly occupied and are not shown.

No	Molecular Orbital electron occupations ^{a)}							
	A _g	B _{1u}	A _g	B _{3u}	B _{2u}	B _{3g}	B _{2g}	B _{1u}
30	2	-	2	-	-	2	2	2
31	2	-	-	2	2	2	2	-
32	2	-	-	2	2	2	-	2
33	2	-	-	2	2	-	2	2
34	2	-	-	2	-	2	2	2
35	2	-	-	-	2	2	2	2
36	-	2	2	2	2	2	-	-
37	-	2	2	2	2	-	2	-
38	-	2	2	2	2	-	-	2
39	-	2	2	2	-	2	2	-
40	-	2	2	2	-	2	-	2
41	-	2	2	2	-	-	2	2
42	-	2	2	-	2	2	2	-
43	-	2	2	-	2	2	-	2
44	-	2	2	-	2	-	2	2
45	-	2	2	-	-	2	2	2
46	-	2	-	2	2	2	2	-
47	-	2	-	2	2	2	-	2
48	-	2	-	2	2	-	2	2
49	-	2	-	2	-	2	2	2
50	-	2	-	-	2	2	2	2
51	-	-	2	2	2	2	2	-
52	-	-	2	2	2	2	-	2
53	-	-	2	2	2	-	2	2
54	-	-	2	2	-	2	2	2
55	-	-	2	-	2	2	2	2
56	-	-	-	2	2	2	2	2

^{a)} Molecular Orbital Symmetry-labels of D_{2h} point group (irreducible representation labels) are listed below.

Table 3. Deviations of Ω -ERG($m=4, M=4$) energies (in hartree) from FCI energies for lowest-energy states ¹⁾ for N₂ (STO-3G basis set, R=2.4 Å). The spatial-symmetry is A_g, point group used is D_{2h}.

Number of RG Sweeps	1	2	3	4
2	0.0051652818	0.0044496662	0.1456535941	0.1590419544
3	0.0013537475	0.0009110845	0.1390419294	0.1583211429
4	0.0005461460	0.0001658260	0.1336763961	0.1579593797
5	0.0002266860	0.0000292291	0.1290447494	0.1574514368
6	0.0000849822	0.0000051067	0.1239403801	0.1533874528
7	0.0000281037	0.0000008789	0.1020435056	0.1146425219
8	0.0000082270	0.0000001576	0.0461757686	0.0592423566
9	0.0000021474	0.0000000371	0.0196591882	0.0253456285
10	0.0000005091	0.0000000119	0.0102294317	0.0124252680
11	0.0000001187	0.0000000041	0.0057474957	0.0083262675
12	0.0000000338	0.0000000014	0.0032838167	0.0067023590
14	0.0000000069	0.0000000001	0.0010890944	0.0049232101
16	0.0000000015	0.0	0.0003529161	0.0036175490
18	0.0000000002	0.0	0.0001118301	0.0025835821
20	0.0	0.0	0.0000355839	0.0017967932
22	0.0	0.0	0.0000118594	0.0012237353
24	0.0	0.0	0.0000043698	0.0008207318
26	0.0	0.0	0.0000018604	0.0005445239
28	0.0	0.0	0.0000009170	0.0003586064
30	0.0	0.0	0.0000005034	0.0002349956
32	0.0	0.0	0.0000002938	0.0001534858
48	0.0	0.0	0.0000000056	0.0000048899

¹⁾ -107.4412958770 h (¹A_g); -107.4350980802 h (⁵A_g); -107.3211561796 h (⁵A_g); -107.3189648501 h (³A_g);

Table 4. Deviations of Ω -ERG($m=4, M=8$) energies (in hartree) from FCI energies for lowest-energy states ¹⁾ for N₂ (STO-3G basis set, R=2.4 Å). The spatial-symmetry is A_g, point group used is D_{2h}.

Number of RG Sweeps	1	2	3	4	5
2	0.0043967655	0.0044496659	0.0023126751	0.1443790153	0.1447959052
3	0.0006285494	0.0009110842	0.0021995496	0.1375120631	0.1377730945
4	0.0001297971	0.0001658189	0.0021932437	0.1319704433	0.1310346840
5	0.0000315033	0.0000289855	0.0021924321	0.1270893953	0.1249041311
6	0.0000077773	0.0000042939	0.0021921720	0.0619839053	0.1090835815
7	0.0000018780	0.0000005661	0.0021920148	0.0134780129	0.1057057533
8	0.0000004440	0.0000000604	0.0021918955	0.0012312488	0.0609172972
9	0.0000001012	0.0000000074	0.0007574603	0.0000004696	0.0216578169
10	0.0000000217	0.0000000009	0.0001767301	0.0000003901	0.0064126635
11	0.0000000043	0.0000000001	0.0000425188	0.0000003242	0.0018273730
12	0.0000000008	0.0	0.0000105175	0.0000002688	0.0005123274
16	0.0	0.0	0.0000000538	0.0000000974	0.0000031019
24	0.0	0.0	0.0000000001	0.0000000013	0.0000000401
32	0.0	0.0	0.0	0.0	0.0000000004

¹⁾ -107.4412958770 h (¹A_g); -107.4350980802 h (⁵A_g); -107.3211561796 h (⁵A_g); -107.3189648501 h (³A_g); -107.3048555744 h (⁵A_g).

Table 5. H₈ (STO-3G basis set, A_g-electronic states). MOs are ordered according to their orbital energies. R = 1.8 Angstrom.

Number of sweeps at convergence	Electronic States (with total energies listed in Hartree)							
	(¹ Ag)	(³ Ag)	(¹ Ag)	(³ Ag)	(⁵ Ag)	(³ Ag)	(¹ Ag)	(¹ Ag)
	-3.8508763833	-3.8118709042	-3.8050317709	-3.7824525753	-3.7803378374	-3.7742870031	-3.7740026177	-3.7632175509
A. Ω-ERG(m, M) cases with $m = M$								
	($m=4, M=4$)							
195	-3.8508763833	-3.8118709041	-3.8050317708	-3.6128049485				
	($m=6, M=6$)							
670	-3.8508763834	-3.8118709042	-3.8050317709	-3.7824525753	-3.7803370847	-3.6128049485		
	($m=8, M=8$)							
590	-3.8508763834	-3.8118709042	-3.8050317709	-3.7824525754	-3.7803378375	-3.7742870029	-3.7740026177	-3.6128049485
B. Ω-ERG(m, M) cases with $m < M$								
	($m=4, M=6$)							
570	-3.8508763834	-3.8118709042	-3.8050317709	-3.7824525753				
	($m=4, M=10$)							
110	-3.8508763833	-3.8118709042	-3.8050317709	-3.7824525753				
	($m=8, M=20$)							
85	-3.8508763833	-3.8118709042	-3.8050317709	-3.7824525753	-3.7803378374	-3.7742870031	-3.7740026177	-3.7632175509

Table 6. The convergence of total energies towards FCI benchmarks for lowest states for C₂ (6-31G basis set, R=1.2 Å / near-equilibrium bond-length) with respect to numbers of RG-sweeps or CI-iterations. The spatial-symmetry is A_g, point group used is D_{2h}. The number of FCI determinants is 414,864. Listed are deviations (in hartree) from the benchmark energies.

Number of RG Sweeps/ CI iterations	Lowest-energy-states			
	1	2	3	4
	(¹ A _g)	(¹ A _g)	(¹ A _g)	(⁵ A _g)
	-75.6334622566	-75.4989339121	-75.4906675380	-75.4278447108
A. Ω-ERG(<i>m</i>=4,<i>M</i>=12)				
1	0.0056488961	0.0126225972	0.0059699226	0.0299441252
2	0.0005814732	0.0019180369	0.0002397105	0.0047105398
3	0.0000462140	0.0001892168	0.0000146908	0.0007061899
4	0.0000029771	0.0000161403	0.0000015834	0.0001189672
B. ALDET-FCI-code				
Size of initial CI guess matrix = 300				
Maximum number of CI expansion vectors = 12				
0	0.0643443455	0.0729367329	0.0702294641	0.0696206823
1	0.0052444593	0.0067304656	0.0052088642	0.0058778593
2	0.0012213197	0.0014662844	0.0009591314	0.0011515286
3	0.0004626358	0.0004242584	0.0002411485	0.0003083555
C. ALDET-FCI-code				
Size of initial CI guess matrix = 3500				
Maximum number of CI expansion vectors = 300				
0	0.0173292843	0.0205454673	0.0198894559	0.0249970849
1	0.0011068623	0.0010911758	0.0009580739	0.0012463549
2	0.0001891335	0.0001584058	0.0001174496	0.0001538430
3	0.0000282955	0.0000223152	0.0000142202	0.0000300668

Table 7. The convergence of total energies towards FCI benchmarks for lowest states for C₂ (6-31G basis set, R=1.8 Å) with respect to numbers of RG-sweeps or CI-iterations. The spatial-symmetry is A_g, point group used is D_{2h}. The number of FCI determinants is 414,864. Listed are deviations (in hartree) from the benchmark energies.

Number of RG Sweeps	Lowest-energy-states		
	1 (¹ A _g)	2 (¹ A _g)	3 (¹ A _g)
	-75.5158646401	-75.5150157586	-75.5056588286
A. Ω-ERG($m=3, M=10$)			
1	0.0103983800	0.0139173727	0.0155096453
2	0.0015540163	0.0025423520	0.0037793127
3	0.0009080528	0.0001146815	0.0012007760
4	0.0003059512	0.0000086333	0.0004486052
5	0.0001002295	0.0000011759	0.0001707232
6	0.0000318861	0.0000001624	0.0000633700
B. Ω-ERG($m=3, M=14$)			
1	0.0105348634	0.0141697302	0.0157741622
2	0.0015706462	0.0022649604	0.0038283200
3	0.0007886201	0.0000611969	0.0012101892
4	0.0002402964	0.0000067008	0.0004508604
5	0.0000782504	0.0000008776	0.0001694785

Figure 1. N₂ (STO-3G basis set). Only five lowest states (A_g) potential energy curves at FCI level of theory at each R value are displayed.

Figure 2. N_2 (STO-3G). Graphical display of the Ω -ERG($m=1, M=4$) convergence rates for the ground-state energy: logarithmic energy error versus the number of RG sweeps for internuclear distances $R=1.2 \text{ \AA}$ ($E=-107.6770854427 \text{ h}$), $1.6 \text{ \AA}$ ($E=-107.5419619206 \text{ h}$) and $2.4 \text{ \AA}$ ($E = -107.4412958770 \text{ h}$).

Figure 3. N_2 (STO-3G, $R = 2.4$ Å). Comparison of total energy convergence rates (A_g -states) for two cases: (Left-panel) Ω -ERG($m=2, M=2$) when two lowest-energy states are kept after each iteration/sweep; (Right-panel) Ω -ERG($m=2, M=3$) when three lowest-energy states are kept after each iteration/sweep. RHF molecular orbitals are ordered according to their energies. The number of target states is $m=2$. See text for details.

Figure 4. H_8 (FCI, STO-3G, A_g -states). Only seven lowest-energy potential energy curves are displayed (black-circles represent singlets, blue-circles represent triplets, and red-circles represent quintuplets). RHF molecular orbitals have been used for FCI calculations (See text).

Figure 5. H_8 ($R = 1.8 \text{ Å}$). Comparison of total energy convergence rates (A_g -states) for two cases: (Left-panel) Ω -ERG($m=4, M=6$) when only six lowest-energy states are kept after each iteration/sweep; (Right-panel) Ω -ERG($m=4, M=20$) when twenty lowest-energy states are kept after each iteration/sweep. The number of target states is $m=4$. RHF molecular orbitals are ordered according to their energies. See text for details.

Figure 6. H_8 ($R = 2.4 \text{ \AA}$, A_g -states). Comparison of Ω -ERG($m=4, M$) energy convergence rates for three cases: (Left-panel) only eight lowest-energy ERG roots ($M=8$) are kept after each iteration/sweep; (Middle-panel) only twelve lowest-energy ERG states ($M=12$) are kept after each iteration/sweep; (Right-panel) only twenty lowest-energy ERG states ($M=20$) are kept after each iteration/sweep. RHF molecular orbitals are ordered according to their energies. See text for details.

Figure 7. H₂O (3-21G, A₁-states). Comparison of logarithmic energy error of Ω -ERG($m=6, M$) energies versus the number of RG sweeps for three cases: (Left-panel) only eight lowest-energy ERG roots ($M=8$) are kept after each iteration/sweep at 2R_e; (Middle-panel) only ten lowest-energy ERG states ($M=10$) are kept after each iteration/sweep at 2R_e; (Right-panel) sixteen lowest-energy ERG states ($M=16$) are kept after each iteration/sweep at 3R_e. Molecular orbitals in FCI calculations are taken from 2-state-averaged CASSCF[8,6]-calculations. See text for details.

Figure 8. H₂O (FCI, 6-31G, A₁-states). Potential Energy Curves for lowest-energy states. Molecular orbitals for FCI calculations are taken from 2-state-averaged CASSCF[8,6]-valence-active-space calculations. Solid circles represent data points obtained from the Ω -ERG(m,M) method (See text for details).

Figure 9. H₂O (6-31G, A_1 -states). Comparison of logarithmic energy error of Ω -ERG($m=6, M=16$) versus the number of RG sweeps for three cases: (Left-panel) at R_e ; (Middle-panel) at $2R_e$; (Right-panel) at $3R_e$. Molecular orbitals in these calculations are taken from 2-state-averaged CASSCF[8,6] valence-active-space calculations. See text for details.