

A hybrid configuration interaction treatment based on seniority number and excitation schemes

Diego R. Alcoba¹, Alicia Torre², Luis Lain^{2,a)}, Ofelia B. Oña³, Pablo Capuzzi¹, Mario Van Raemdonck⁴, Patrick Bultinck⁴, and Dimitri Van Neck⁵

¹*Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires and Instituto de Física de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas. Ciudad Universitaria, 1428 Buenos Aires, Argentina*

²*Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco. Apdo. 644 E-48080 Bilbao, Spain*

³*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Universidad Nacional de La Plata, CCT La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas. Diag. 113 y 64 (S/N), Sucursal 4, CC 16, 1900 La Plata, Argentina*

⁴*Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Gent, Belgium*

⁵*Center for Molecular Modelling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium*

We present a configuration interaction method in which the Hamiltonian of an N -electron system is projected on Slater determinants selected according to the seniority-number criterion along with the traditional excitation-based procedure. This proposed method is especially useful to describe systems which exhibit dynamic (weak) correlation at determined geometric arrangements (where the excitation-based procedure is more suitable) but show static (strong) correlation at other arrangements (where the seniority-number technique is preferred). The hybrid method amends the shortcomings of both individual determinant selection procedures, yielding correct shapes of potential energy curves with results closer to those provided by the full configuration interaction method.

^{a)} Author to whom correspondence should be addressed. Electronic mail: qfplapel@lg.ehu.es

I. INTRODUCTION

It is well known that the full configuration interaction (FCI) method provides the exact solutions of the Schrödinger equation for an N -electron system in a given Hilbert space. Unfortunately, its factorial growth with respect to the number of electrons and the number of basis set orbitals demands a prohibitive computational cost. One of the most popular approaches used to reduce this computational cost is to limit the number of Slater determinants in the configuration space; this idea constitutes the foundation of the configuration interaction (CI) methods. This technique requires to select, according to a determined criterion, the Slater determinants in which the N -electron Hamiltonian is projected. Most often, this selection is performed in terms of the number of spin-orbitals excited with respect to a given reference determinant. However, more recently an alternative CI procedure has been proposed; in this case the selection of the Slater determinants is accomplished according to the seniority number of the determinants used to project the Hamiltonian¹⁻⁵ (the seniority number has been defined as the number of singly occupied orbitals in a determinant).^{6,7} On the other hand, the electronic correlation energy is usually decomposed into two components which have been denominated as dynamic (weak) and static (strong) correlations.⁸⁻¹² The correlation is essentially dynamic when a single-determinant reference is a good zeroth-order wave function. The static (nondynamic) correlation is important in systems with strong multireference character and necessarily requires the use of wave functions composed of multiple Slater determinants, even for suitable zeroth-order descriptions. Systems with near-degenerate ground states, molecules with stretched bonds, radicals, complexes of transition metals and so forth are examples which fit this correlation model, which has also been found in bond-breaking processes and in the description of superconductivity and other properties of materials.

The performance of both excitation- and seniority-number-based selection criteria in CI expansions to describe N -electron systems has been tackled in Ref. 1 which reports studies of atoms and molecular species in which either dynamic or static correlation is dominant. The conclusions reported in that reference indicate that the

excitation-based configuration selection procedure is more efficient than the seniority-based approach when the system presents essentially dynamic correlation. However, in those situations where the static correlation is important, the seniority-number-based selection procedure leads to better results. In the description of dissociation processes or bond breaking, one often finds molecular systems that show mainly dynamic correlation at arrangements near the equilibrium distances but present static correlation at stretched arrangements. A global study of such systems raises the problem of choosing one of these two above mentioned CI expansion construction criteria. The aim of this work is to propose a method that combines both CI expansion types, providing a framework that accounts efficiently for both types of correlation. In our procedure, the N -electron Hamiltonian is projected on a set of Slater determinants which possess a determined seniority number plus the additional Slater determinants needed to complete a given excitation level with respect to a reference. The method turns out to be suitable to describe any system and is especially useful for wave functions which undergo dramatic changes in the dominances of the Slater determinants as a consequence of the stretching of the internuclear distances within molecular systems.

This work has been organized as follows. In Sec. II we review the main theoretical aspects involved in the proposed methodology, indicating the formulation of the N -electron seniority number operator by means of the spin-free second-order replacement operators and the features of the CI expansions. Section III reports the computational details as well as the criteria followed to select the molecular orbital basis to perform this treatment. In Sec. IV we show results obtained from the proposed hybrid method; in this work the treatment involves all Slater determinants whose seniority number is zero, augmented with those of the single and double excitation configuration interaction (CISD) method not yet included. These results have been compared with those arising from the seniority-number approach (at zeroth seniority-number level), with those of the CISD or single, double and triple excitation configuration interaction (CISDT) methods and with those of the FCI procedure. This Section also reports the number of Slater determinants required in each method, in order to assess the computational

expense. Finally, in Sec. V we summarize the main conclusions of this work.

II. THEORETICAL REVIEW

The N -electron seniority number operator $\hat{\Omega}$ can be formulated by means of the spin-free replacement operators as²

$$\hat{\Omega} = \sum_{i=1}^K (\hat{E}_i^i - \hat{E}_{ii}^{ii}) \quad (1)$$

in which $\hat{E}_i^i = \sum_{\sigma} a_{i\sigma}^{\dagger} a_{i\sigma}$ and $\hat{E}_{ii}^{ii} = \sum_{\sigma_1, \sigma_2} a_{i\sigma_1}^{\dagger} a_{i\sigma_2}^{\dagger} a_{i\sigma_2} a_{i\sigma_1}$ are the spin-free first- and second-order replacement operators respectively.¹³⁻¹⁵ In this formalism $a_{i\sigma}^{\dagger}$ and $a_{i\sigma}$ denote the standard creation and annihilation fermion operators corresponding to a spin-orbital i^{σ} , where $\sigma = \alpha, \beta$ means the spin coordinate and i represents an orbital of an orthonormal basis set composed of K functions. According to Eq. (1), the expectation value of the operator $\hat{\Omega}$ for an N -electron Slater determinant $\langle \hat{\Omega} \rangle = \Omega$ is the difference between the total number of electrons N (i.e. $\sum_{i=1}^K \langle \hat{E}_i^i \rangle$) and the number of electrons corresponding to doubly occupied orbitals in the determinant ($\sum_{i=1}^K \langle \hat{E}_{ii}^{ii} \rangle$). In other words, Ω is a positive integer meaning the number of unpaired electrons in the determinant.

The N -electron Slater determinants constructed with K basis functions and a determined spin quantum number S_z can be classified according to the values $\Omega = 0, 2, 4 \dots$ (for N even) or $\Omega = 1, 3, 5 \dots$ (for N odd), satisfying the constraint condition $\Omega \geq 2|S_z|$. In both cases, the maximum value of the Ω quantity is $\Omega_{\max} = N$ (if $K \geq N$) or $\Omega_{\max} = 2K - N$ (if $K < N$). The projection of the Hamiltonian operator corresponding to an N -electron system on one or more sets of determinants (each set including all determinants with a given Ω value) yields an N -electron CI Hamiltonian matrix. The diagonalization of this matrix provides the eigenvalues and eigenvectors which are the energies and wave functions of the seniority-number-based CI method at levels $\Omega = 0, 2, 4 \dots$ or $\Omega = 1, 3, 5 \dots$. In the limit, when all possible values of Ω are taken into account ($\Omega = 2|S_z|, 2(|S_z| + 1), \dots, \Omega_{\max}$) the seniority-number-based CI

energies and wave functions coincide with those arisen from the FCI method, which utilizes all possible determinants with a particular S_z value, constructed with the K functions, to perform the Hamiltonian projection. This CI(Ω) procedure constitutes an alternative to the traditional one, in which the classification of the Slater determinants to project the Hamiltonian is implemented according to the excitation levels with respect to a reference determinant.^{16–19} Both CI approaches lead to different energies, although they converge to the FCI result when a high number of determinants is used in the numerical determinations. Furthermore, a basis-set transformation yields changes in the results arising from both CI methods⁴ what makes it necessary to properly select the type of molecular orbitals leading to more efficient wave function expansions.^{1,4,20,21}

The concept of seniority number has also been extended to N -electron spin-adapted wave functions $\Psi(N, S)$ with a given spin quantum number S and any S_z .² In this case, the expectation value of the seniority number is

$$\langle \hat{\Omega} \rangle_{\Psi(N,S)} = \langle \Psi(N, S) | \hat{\Omega} | \Psi(N, S) \rangle = \sum_i {}^1D_i^i - 2 \sum_i {}^2D_{ii}^{ii} \quad (2)$$

in which ${}^1D_i^i = \langle \Psi(N, S) | \hat{E}_i^i | \Psi(N, S) \rangle$ and ${}^2D_{ii}^{ii} = \frac{1}{2} \langle \Psi(N, S) | \hat{E}_{ii}^{ii} | \Psi(N, S) \rangle$ are elements of the spin-free first- and second- order reduced density matrices respectively, corresponding to the wave function $\Psi(N, S)$. In this formulation the S_z quantum number has been omitted, since these matrix elements are independent of the spin projection. The expectation value $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ is no longer an integer like in a determinant case but a quantity depending on the nature of the i orbitals. In Refs. 2 and 4 we have proposed to perform transformations of the molecular basis set so that the expectation value of the seniority number operator for a FCI state, $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$, gets a minimum value. The computational procedure we have used, based on the method reported by Subotnik *et al.*,²² allows one to obtain more compact FCI wave functions and CI wave functions attaining larger correlation energies. The orbitals resulting from that minimization have been denominated M_{\min} in contrast to the natural orbitals (NO) and the Hartree-Fock canonical molecular orbitals (CMO). The functions that constitute the

basis sets M_{\min} are not, in general, symmetry-adapted orbitals although the molecular symmetry can be restored. Other applications of the expectation value $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ arise from its relationship with the effectively unpaired electron number corresponding to the state $\Psi(N, S)$.^{23,24}

As has been mentioned in the Introduction, the excitation-based and the seniority-number-based CI expansions present advantages and deficiencies respectively to describe systems requiring a simple determinant as zeroth-order wave functions, but both of them show the opposite behavior when multideterminantal wave functions are needed at this level of approximation.¹ There are ambiguous situations in which a system is suitably described by expansions with a very strong dominance of a Slater determinant at a determined geometrical arrangement but requires several Slater determinants at other arrangements. Consequently, it seems reasonable to study the performance of the Hamiltonian projection on the union of the sets of determinants from the seniority-number-based and excitation-based CI methods (at given Ω and excitation levels). This configuration space is wider than that constituted by each CI method individually and necessarily provides better results at any geometrical arrangement. CI expansions of hybrid character based on excitations and other features of the determinants (energies) have also been recently proposed.²⁵ In the next sections we describe results drawn out at several geometrical arrangements of systems which present marked changes in the dominances of the Slater determinants.

III. COMPUTATIONAL DETAILS

The reliability of our methodology has been tested by determining ground-state electronic energies in closed-shell atomic and molecular systems using the hybrid CI scheme. We have projected the Hamiltonian of these systems on the union of the Slater determinant sets required in the $\text{CI}(\Omega = 0)$ and CISD procedures, what has been denoted as $\text{CI}_{\text{SD}}^{(\Omega=0)}$. The dimensions of this N -electron Hamiltonian matrix is $\sum_{i=0}^2 \sum_{p=0}^i \binom{K-\frac{N}{2}}{p} \binom{\frac{N}{2}}{p} \binom{K-\frac{N}{2}}{i-p} \binom{\frac{N}{2}}{i-p} + \binom{K}{\frac{N}{2}} - [\frac{N}{2}(K - \frac{N}{2}) + 1]$, in which the first term is the CISD Hamiltonian matrix size, the second term is the dimension of the $\Omega = 0$

Hamiltonian matrix and the last one in the number Slater determinants belonging to both spaces. The results have been compared with those arising from the individual CI($\Omega = 0$), CISD and CISDT procedures, as well as with those provided by the FCI method. The excitation level of the determinants used in the CISD, CISDT, etc, procedures has been evaluated with respect to a single reference determinant. In the molecular calculations we have used small basis sets in order to get FCI results at an affordable cost. The basis sets utilized for each system have been indicated in the tables and figures in the next section. We have carried out the corresponding basis set transformations so that finally the N -electron CI matrices have been expressed in the M_{\min} orbitals in which the expectation values $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ attain the minimum values for the FCI procedure.⁴ Experimental equilibrium bond lengths and angles and symmetrically stretched configurations have been used to describe potential energy curves in the molecular systems. The one- and two-electron integrals required to construct the N -electron CI matrices have been obtained from a modified version of the PSI 3.3 package.²⁶ We have also used that code to calculate the Hartree-Fock CMOs utilized as initial basis in the iterative procedure which determines the M_{\min} basis sets. In subsequent steps we have elaborated our own codes to perform the basis set transformations and to construct the N -electron CI($\Omega = 0$), CISD, $CI_{SD}^{(\Omega=0)}$ and CISDT matrices; this last task has been implemented using the algorithms in the programmes developed for Refs. 27 and 28.

IV. RESULTS AND DISCUSSION

Table I gathers energy values of selected atomic systems arising from the CI($\Omega = 0$), CISD, $CI_{SD}^{(\Omega=0)}$, CISDT and FCI methods, as well as their computational cost. This cost has been reflected by means of the number of Slater determinants in the Hamiltonian projections. This table also shows the Gaussian basis sets used in these numerical determinations although all values reported in this table have been obtained from the corresponding M_{\min} orthonormal orbital basis. The Be atom has been chosen as prototype of system having a marked static correlation;¹ in fact the CI($\Omega = 0$) result is

close to the CISD one with lower computational cost (only 91 Slater determinants). The hybrid $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method, proposed in this work, leads to a better result being very close to that provided by the CISDT procedure with a markedly lower computational cost (823 Slater determinants vs 3925 ones). The correlation energy in the Ne atom has been considered to be purely dynamic;¹ our results confirm this behavior since the $\text{CI}(\Omega = 0)$ result is no longer close to the CISD value as in the Be case. However, the hybrid $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method yields a value quite close to that of the CISDT method at lower computational cost and in the F^- case (a system isoelectronic with the Ne atom) the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ value turns out to be even lower than that obtained from the CISDT procedure. The systems Mg and Al^+ can be classified between those possessing an intermediate strength of static correlation energy; the hybrid $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method also predicts satisfactory results for these systems. The results found for the Ar atom show that this system presents a behavior similar to that of the Ne atom; both atoms possess essentially dynamic correlation, as expected.

In Figs. 1, 2 and 3 we show potential energy curves of the symmetrically stretched systems BeH_2 and H_2O as well as that of the N_2 molecule. Our aim is to assess the performance of the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method by comparing its results and computational cost with those arising from the more known $\text{CI}(\Omega = 0)$, CISD and FCI procedures. Each numerical value described in these curves has been obtained using the basis set M_{min} in which the $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ quantity gets a minimum value for the corresponding FCI wave function $\Psi(N, S)$. The accuracy of the potential energy curves obtained from the CI methods with respect to the FCI one is compared in Table II, where the maximum absolute errors (MAE) and nonparallelity errors (NPE) are shown for each method. As can be observed, the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method decreases these quantities in one and two orders of magnitude for the BeH_2 and H_2O systems and near one order of magnitude for the N_2 molecule. The computational cost of these numerical determinations has been reflected in Table III in terms of the number of Slater determinants required in each method. A survey of the BeH_2 curve shapes described in Fig. 1 shows very good agreement for all studied methods at near-equilibrium distances. However, at longer

internuclear distances, where static correlation is higher, the $\text{CI}(\Omega = 0)$ method exhibits a hump, which has also been reported and discussed in other systems,¹ although near the dissociation this curve converges to the FCI one. This hump is no longer present in the results yielded by the hybrid $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method which requires only a little more computational effort compared to the CISD procedure. As expected, the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method agrees better with the FCI one in the whole interval of internuclear distances studied. Fig. 2 describes the potential energy curves of the H_2O molecule. As can be observed, the results from the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method are near coincident with the FCI ones both for near-equilibrium geometries as well as for distances close to the dissociation limit, although the computational cost is only slightly higher than the CISD one. In Fig. 3 we show the results corresponding to the N_2 molecule in which we appreciate the crossing between the $\text{CI}(\Omega = 0)$ and CISD curves. The CISD values are closer to the FCI ones than those of $\text{CI}(\Omega = 0)$ method at the near-equilibrium region (low static correlation) but this behavior is quite opposite at the dissociation limit region (high static correlation). Similarly to the BeH_2 and H_2O molecules, the performance of the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ curve in the N_2 system is better than those provided by the $\text{CI}(\Omega = 0)$ and CISD methods individually and its computational cost is only slightly higher than that required by the CISD procedure.

We have studied the behavior of the results provided by the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method using molecular orbital basis sets other than the M_{min} ones. In Figs. 4 and 5 we have represented potential energy curves of the symmetrically stretched H_2O molecule using the NO and CMO basis sets respectively. As can be seen by comparing Figs. 2 and 4, the $\text{CI}(\Omega = 0)$ results are closer to the FCI ones in the M_{min} basis set, in agreement with the conclusions reported in Ref. 4, providing better results than the CISD ones. However the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ curve with the NO basis set (Fig. 4) is just as nearly coincident with the FCI one as the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ curve with the M_{min} basis (Fig. 2). The results arising from the use of the CMOs, shown in Fig. 5, also indicate the closeness of the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ curve to the FCI one. From a computational point of view, the CMO basis sets are more easily available than the NO and M_{min} ones, and consequently they could be

preferably used within the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ scheme, avoiding the FCI determinations. Fig. 5 also shows the presence of a small hump in the curves $\text{CI}(\Omega = 0)$, CISD and $\text{CI}_{\text{SD}}^{(\Omega=0)}$ in the CMO basis set, which does not appear in their counterparts calculated in the NO and M_{min} basis sets. **However, the hump in the CMO curves gets its smallest size in the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ method. In order to elucidate whether the hump is an artefact of using a minimal basis set, we also performed calculations using the split valence 6-31G basis set, revealing indeed that the use of a larger basis set leads to the disappearance of this hump (see Fig. 6). Also note that all main features reported for the STO-3G data remain for the larger basis set.**

Truncated methods, i.e. methods other than FCI one, suffer from an undesirable dependence on the basis chosen, as is clearly demonstrated above. We therefore also performed preliminary calculations at $\text{CI}_{\text{SD}}^{(\Omega=0)}$ level, with an energy optimized single particle basis to examine the magnitude of the further change in energy compared to the energies obtained using the other molecular orbital bases. We have chosen the N_2 molecule as a prototype system. Although a detailed description of the algorithm used and more detailed examinations of this effect will be presented in future work, Fig. 7 clearly shows that the energy optimized basis set slightly improves on the energies calculated using the NO and M_{min} basis sets, and that these energies are better than those given by the CMO basis set although their respective order may differ along the bond stretching coordinate. The key conclusion of the paper, is however confirmed in all cases: as shown in Fig. 8, the union of the $\text{CI}(\Omega = 0)$ and CISD determinant sets lowers significantly the energies provided by those procedures individually without an important increase in computational cost.

V. CONCLUDING REMARKS AND PERSPECTIVES

In this work, we have proposed a new procedure which possesses a hybrid character within the CI technique framework. The method is based on the projection of an N -electron Hamiltonian on the union of two Slater determinant sets, each of them constituted according to a different criterion. One of these sets is composed of all Slater

determinants up to a determined seniority number; the other set is composed of a reference determinant and its excitations up to a determined level. We report numerical determinations on selected atomic and molecular systems using a simple version of the hybrid method, the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ one. Its results and computational cost are compared with those obtained from its parents $\text{CI}(\Omega = 0)$ and CISD methods. Our proposal turns out to be particularly useful to describe systems which undergo strong changes in the static correlation energies at stretched geometries with respect to near-equilibrium arrangements, correcting the deficiencies of the $\text{CI}(\Omega = 0)$ and CISD procedures. Notably, the sets of the $\text{CI}(\Omega = 0)$ and the CISD Slater determinants act like ideal complements to each other, solving many of the issues related to strong static correlation. The NO and M_{min} basis sets are optimal for the traditional and seniority-type CI procedures respectively from a compactness of wave function perspective, and consequently we have considered these basis sets in our calculations. Our best results have been obtained using the M_{min} molecular orbital basis sets, which minimizes the seniority number for the FCI procedure. However, we also show that other molecular basis sets, as those of CMOs, improve the $\text{CI}(\Omega = 0)$ and CISD results with lower computational costs. One can also find the optimal molecular orbital basis sets for any CI-type method from an energy perspective. We also report preliminary calculations with a $\text{CI}_{\text{SD}}^{(\Omega=0)}$ energy optimized molecular orbital basis set pointing out a further energy lowering. Work along this line is being pursued in our laboratories.

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TABLE I: Values of energies, computational cost and basis sets utilized for atomic systems calculated at different levels of CI methods. Results were obtained using the orthonormal basis that minimizes the seniority number for the FCI procedure (M_{\min}).

system	basis	No. determinants						Energy/ E_h			
		CI($\Omega = 0$)	CISD	CI $_{SD}^{(\Omega=0)}$	CISDT	FCI	CI($\Omega = 0$)	CISD	CI $_{SD}^{(\Omega=0)}$	CISDT	FCI
Be	cc-pVDZ	91	757	823	3925	8281	-14.617064	-14.617355	-14.617365	-14.617393	-14.617409
F ⁻	cc-pVDZ	2002	2836	4792	36916	4008004	-99.430350	-99.553918	-99.555046	-99.554522	-99.560772
Ne	cc-pVDZ	2002	2836	4792	36916	4008004	-128.551000	-128.675320	-128.676110	-128.676430	-128.680896
Mg	6-31G	1716	2479	4152	30339	2944656	-199.627920	-199.630130	-199.630160	-199.630240	-199.630374
Al ⁺	6-31G	1716	2479	4152	30339	2944656	-241.690140	-241.692590	-241.692620	-241.692690	-241.692805
Ar	6-31G	715	1801	2479	18025	511225	-526.784570	-526.812090	-526.812220	-526.812690	-526.813352

TABLE II: Maximum absolute errors (MAE) and nonparallelity errors (NPE) (in mE_h) of the CI potential energy curves with respect the FCI one. Results were obtained using the orthonormal basis set that minimizes the seniority number for the FCI procedure (M_{\min})

	CI($\Omega = 0$)	CISD	CI _{SD} ^($\Omega=0$)
	MAE NPE	MAE NPE	MAE NPE
BeH ₂	68.60 65.73	35.05 34.61	8.12 7.84
H ₂ O	19.53 12.85	66.69 66.60	0.19 0.17
N ₂	84.79 40.75	147.1 143.3	47.71 45.18

TABLE III: Computational cost reflected in the size of the Slater determinant basis for molecular systems calculated at different levels of CI methods.

		No. determinants			
system	basis	CI($\Omega = 0$)	CISD	CI _{SD} ^($\Omega=0$)	FCI
BeH ₂	STO-3G	35	205	227	1225
H ₂ O	STO-3G	21	141	151	441
N ₂	STO-3G	120	610	708	14400

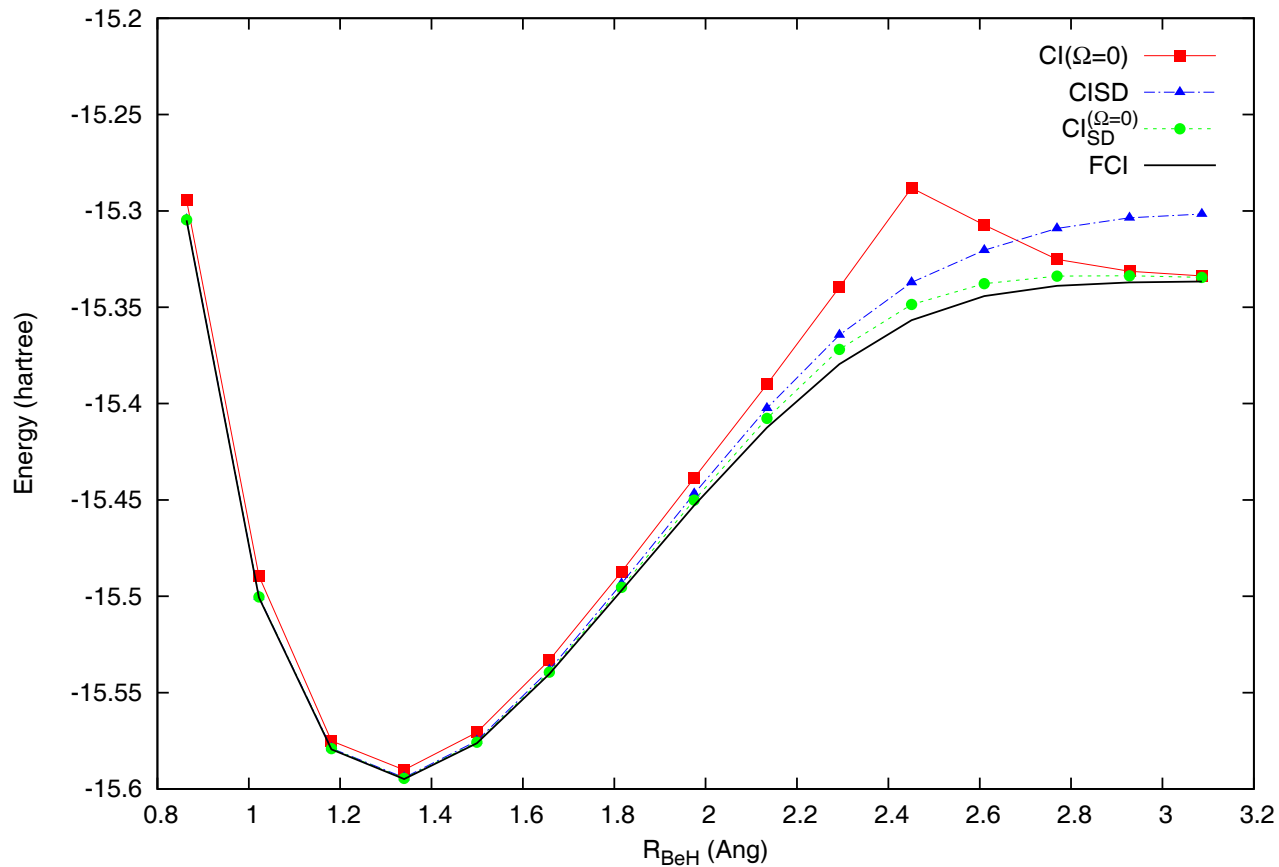


FIG. 1: Potential energy curves for the symmetric dissociation of the BeH_2 molecule using STO-3G basis set transformed to the basis which minimizes the seniority number for the FCI procedure (M_{min}).

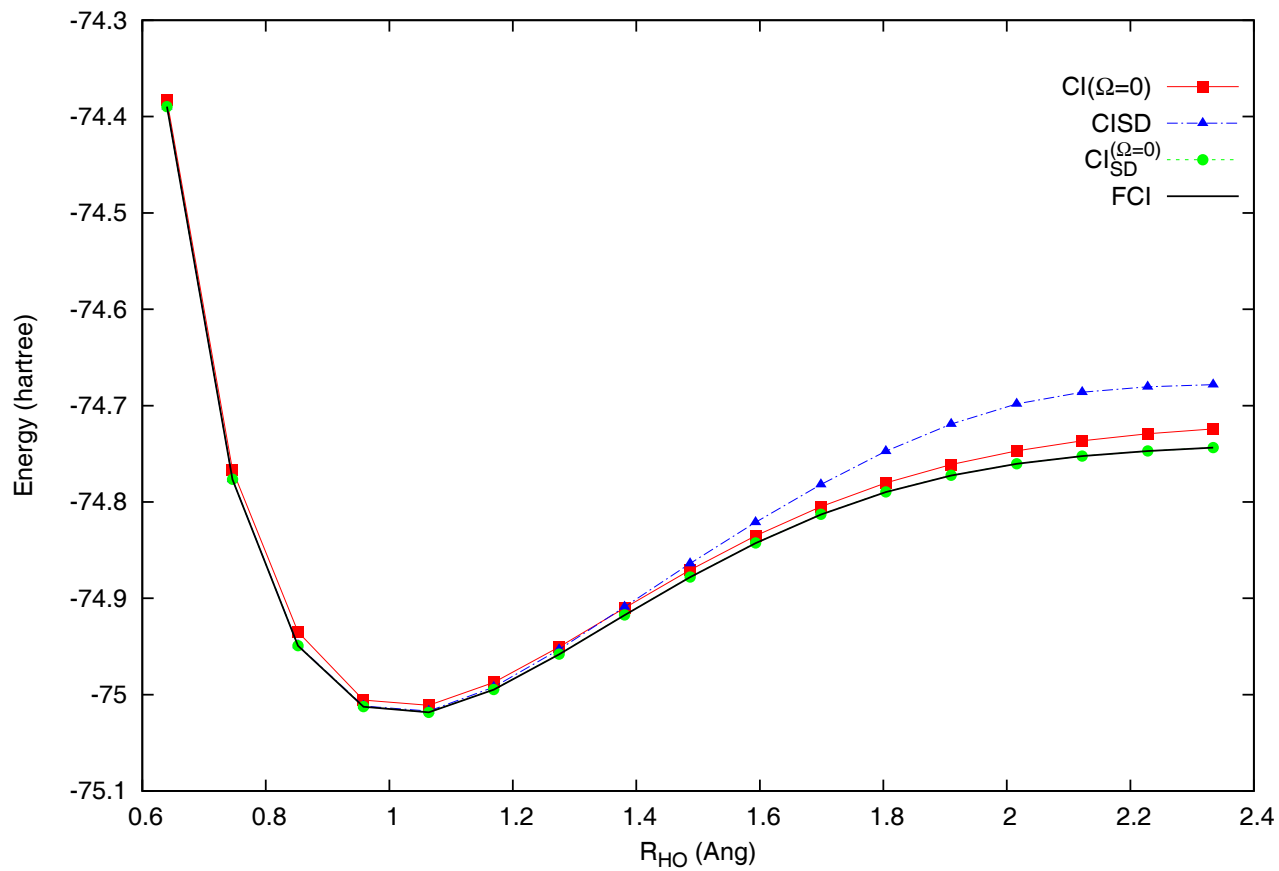


FIG. 2: Potential energy curves for the symmetric dissociation of the H₂O molecule using STO-3G basis set transformed to the basis which minimizes the seniority number for the FCI procedure (M_{\min}).

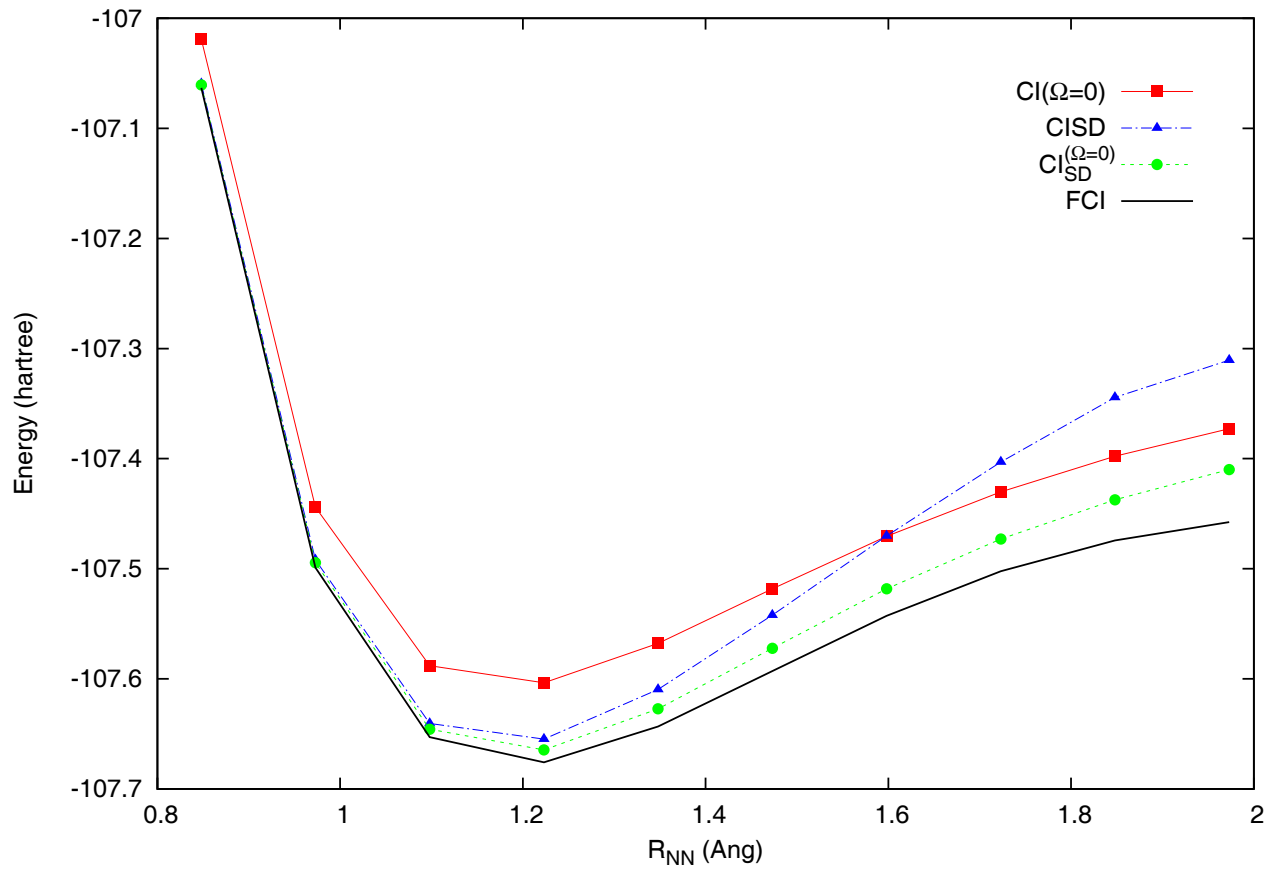


FIG. 3: Potential energy curves for the dissociation of the N₂ molecule using STO-3G basis set transformed to the basis which minimizes the seniority number for the FCI procedure (M_{\min}).

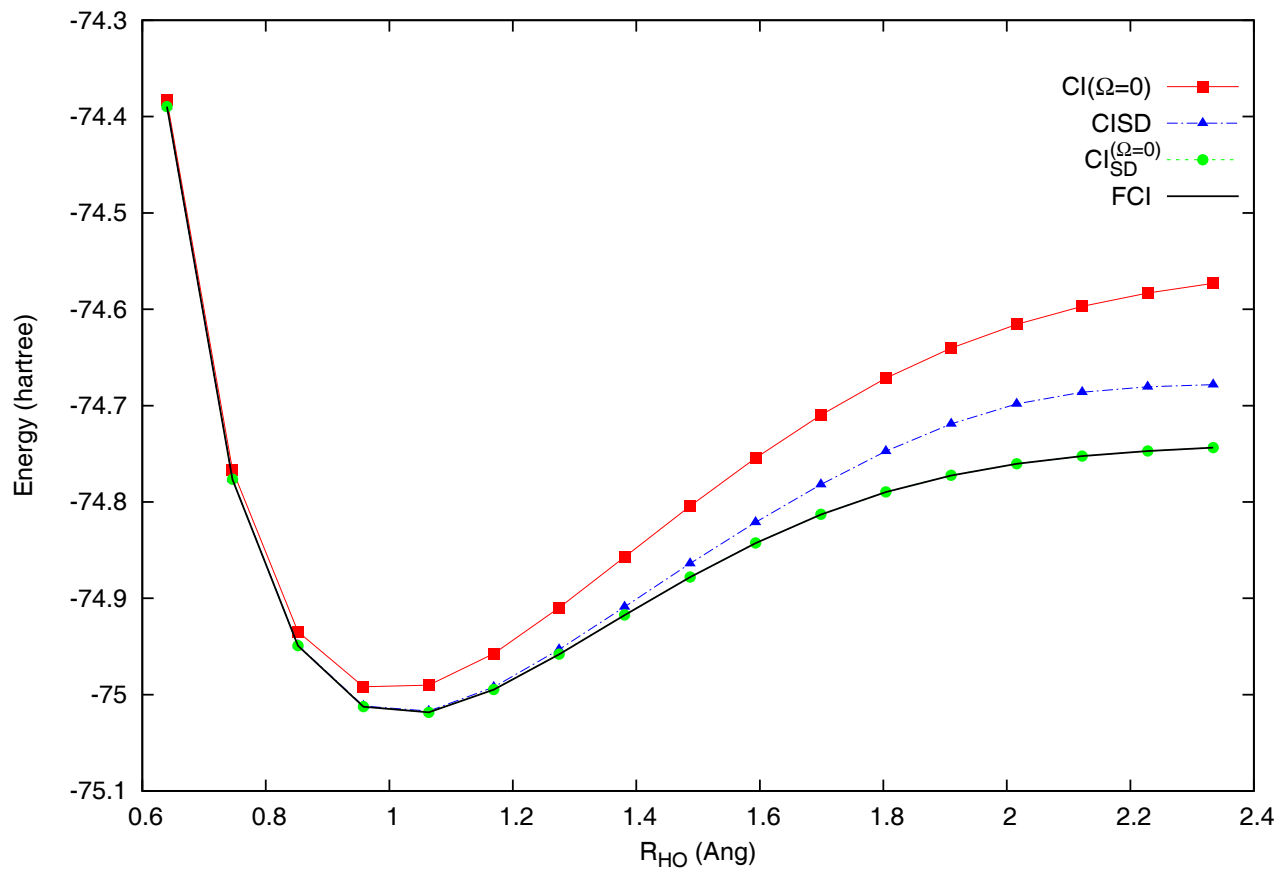


FIG. 4: Potential energy curves for the symmetric dissociation of the H₂O molecule using STO-3G basis set transformed to the natural orbital (NO) set which diagonalize the FCI first-order reduced density matrix.

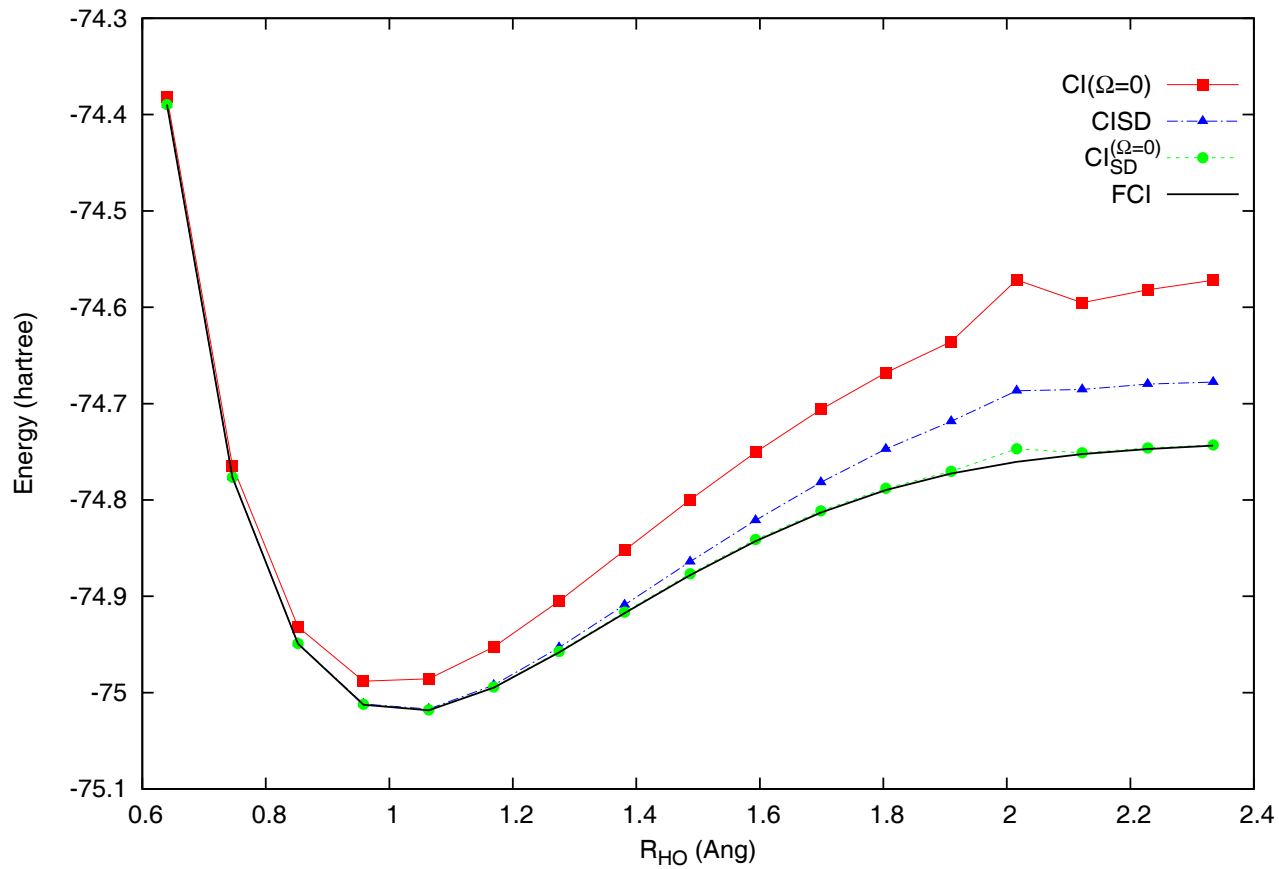


FIG. 5: Potential energy curves for the symmetric dissociation of the H₂O molecule using STO-3G basis set transformed to the Hartree-Fock canonical molecular orbital (CMO) set.

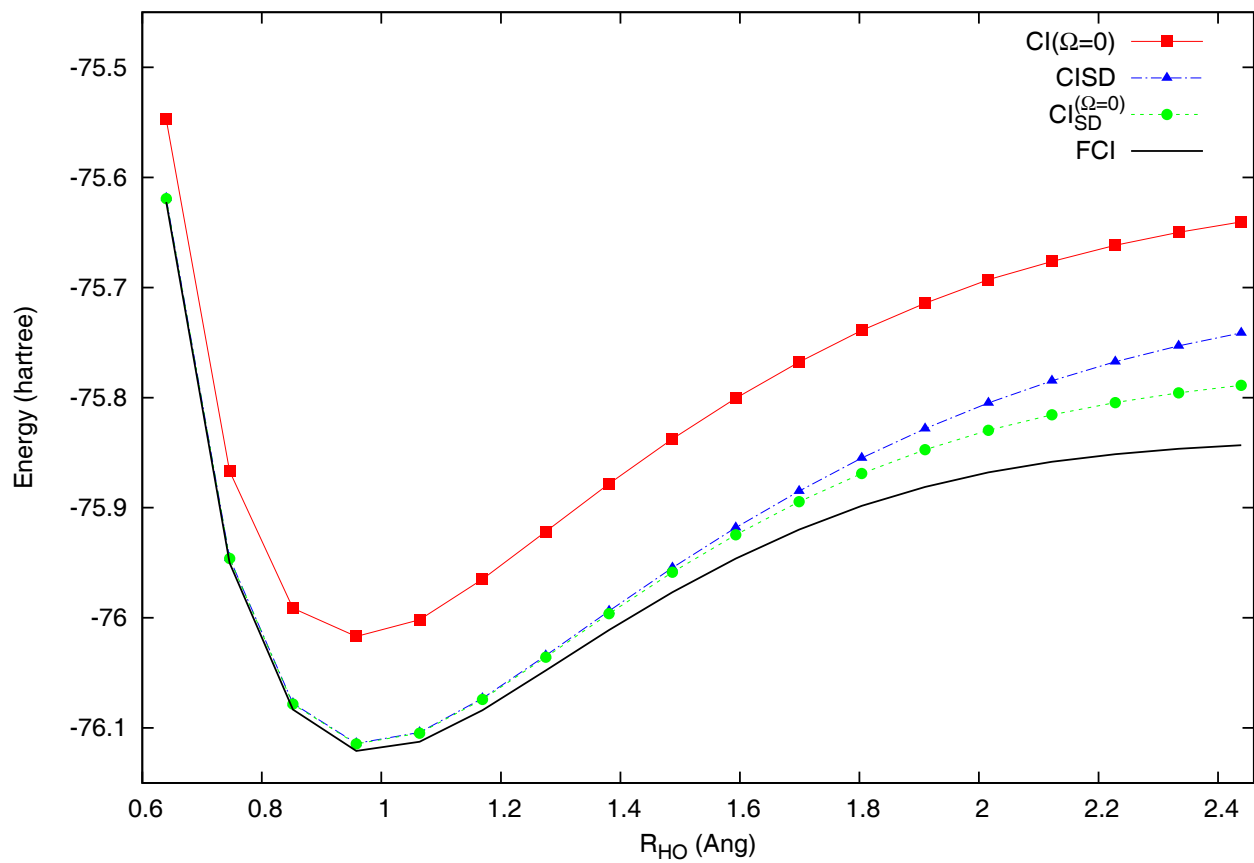


FIG. 6: Potential energy curves for the symmetric dissociation of the H₂O molecule using 6-31G basis set transformed to the Hartree-Fock canonical molecular orbital (CMO) set.

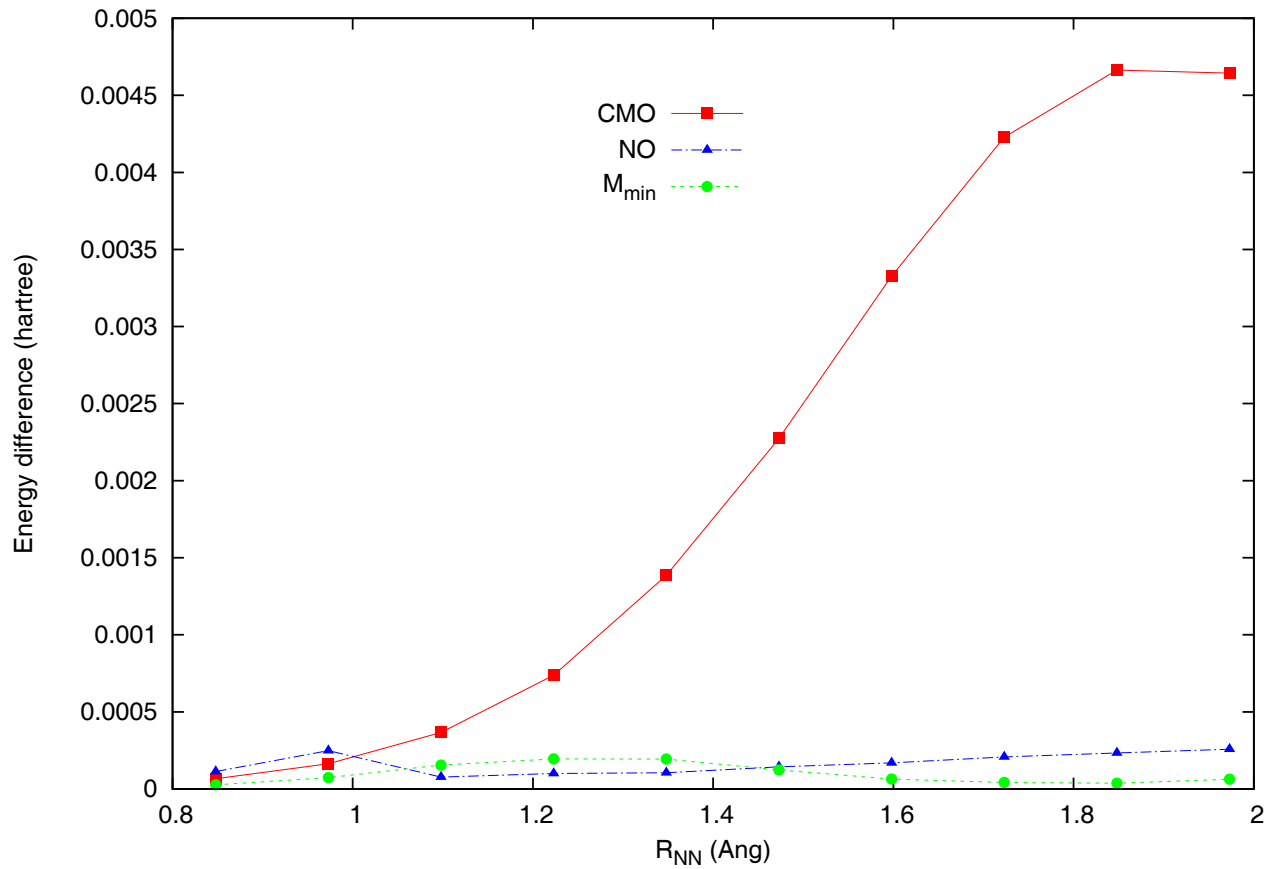


FIG. 7: $CI_{SD}^{(\Omega=0)}$ energy differences with respect to the energy optimized basis set for different single particle bases as a function of internuclear distance in the N_2 molecule.

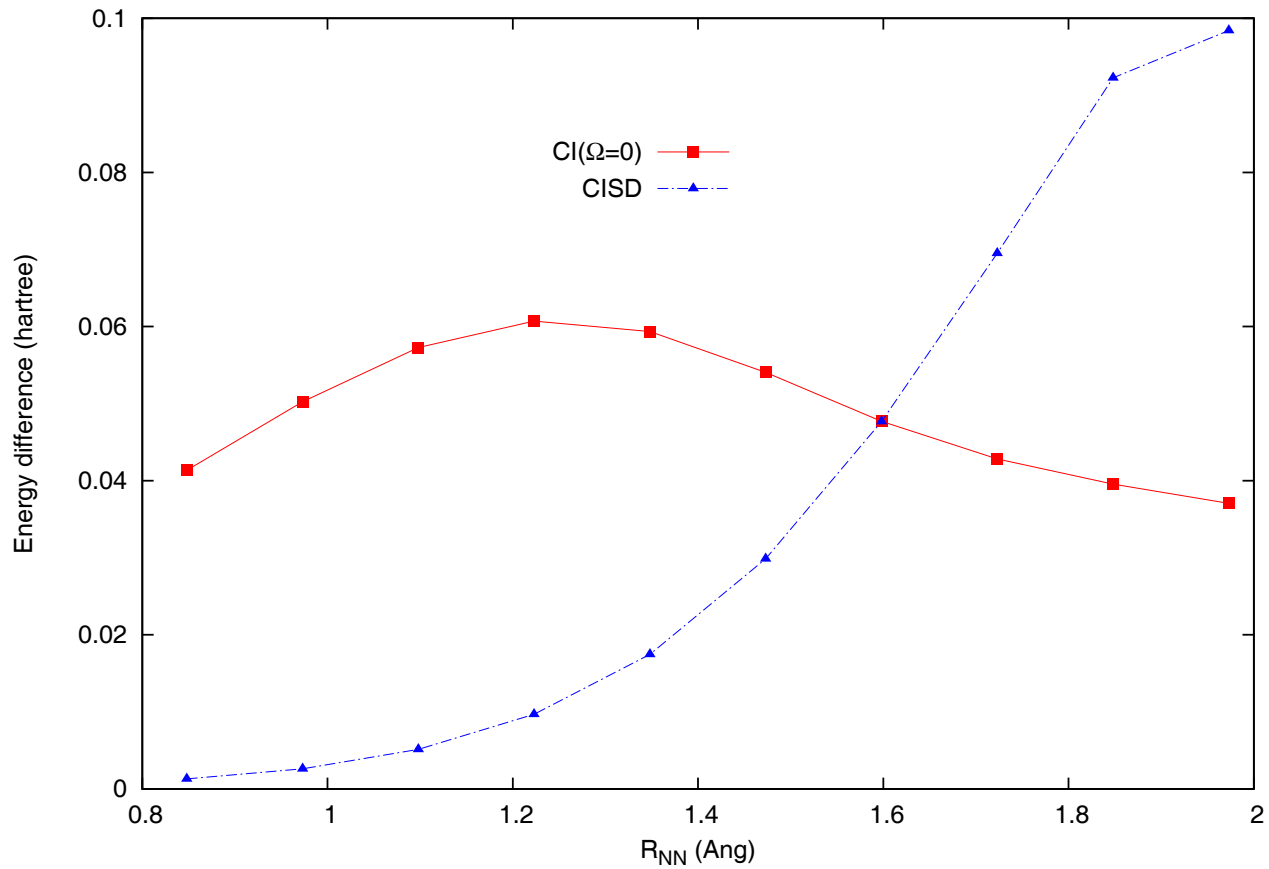


FIG. 8: Energy differences for CI($\Omega = 0$) and CISD methods with respect to the $\text{CI}_{\text{SD}}^{(\Omega=0)}$ model using energy optimized orbitals for each method as a function of internuclear distance in the N_2 molecule.