



Research paper

Natural transition orbitals for the calculation of correlation and excitation energies

Sebastian Höfener*, Wim Klopper

Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), P.O. Box 6980, D-76049 Karlsruhe, Germany



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ABSTRACT

We propose a scheme to reduce the virtual space in the second-order approximate coupled-cluster singles-and-doubles (CC2) method, allowing for an accurate description of both ground-state correlation and excitation energies. A set of natural virtual orbitals is constructed using the ground-state MP2 density as well as the configuration-interaction-singles (CIS) excitation vectors. The results show that approximately half of the virtual space can be removed while an accuracy of about 90% for conventional correlation energies is obtained. CC2 excitation energies show in most cases an error of about 2% or less when the virtual space is reduced to half.

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1. Introduction

Due to the scaling of correlation methods with basis-set size, many attempts have been made to truncate the size of the virtual orbital space not only for ground-state methods but also for response-property calculations. While first ideas concerning natural orbitals reach back to the 1950s [1–6], in 1997 it was shown by Klopper et al. that natural orbitals based on the second-order Møller-Plesset (MP2) density can provide >90% of the ground-state coupled-cluster singles and doubles (CCSD) correlation energy when using the occupation numbers of the natural virtual orbitals to remove half of the virtual space [7]. Some years later excitation vectors obtained from the configuration-interaction-singles (CIS) method were used to set up domains for coupled-cluster methods using localized orbitals [8,9]. Pair-natural orbitals (PNOs) [10–14] and orbital-specific virtual (OSV) orbitals have been (re) discovered and applied by many authors more recently to coupled-cluster methods [15–20] as well as to the random-phase approximation [21]. These methods are able to significantly reduce the virtual space and thus yield dramatically reduced computation times. However, a drawback of several methods is that the efficiency comes at the cost of non-orthonormal orbital sets for different orbital pairs and excited states, requiring special implementations. To circumvent this, a restricted-virtual space (RVS) approach was suggested by Send et al. who reduced the virtual space drastically using only the canonical virtual orbitals with orbital energies below 50 eV [22]. This method provides accurate

excitation energies in many cases but ground-state correlation energies as well as frequency-dependent dipole polarizabilities using coupled-cluster theory can exhibit large errors [23] and it can lead to increased errors for $n\pi^*$ or $\pi\sigma^*$ states using ADC(2) [24].

In the present work, we construct effective natural transition orbitals (NTOs) suited for both ground and excited states *via* combining the ground-state MP2 density with CIS excitation vectors and a subsequent diagonalization of the virtual-virtual block of the so-obtained Fock matrix to form canonical orbitals. To the best of our knowledge, such a scheme is applied for the first time to calculate G_0W_0 quasi-particle energies. As an excited state property, we investigate oscillator strengths obtained at the second-order approximate coupled-cluster singles-and-doubles (CC2) level of theory [25].

2. Method

In order to reduce the space of virtuals efficiently, the key step is to combine appropriate measures for ground-state correlation energies and excitation energies, from which those virtual orbitals are extracted which belong to occupation numbers above a certain threshold. In the following, we discuss three methods to construct effective virtual spaces suited for both ground and excited states with a subsequent diagonalization of the so-obtained Fock matrix to form canonical orbitals.

2.1. Ground-state density

For coupled-cluster methods using single and double excitations, it was shown by Klopper et al. that correlation calculations using only the natural virtual orbitals of the unrelaxed virtual-

* Corresponding author.

E-mail addresses: sebastian.hoefener2@kit.edu (S. Höfener), klopper@kit.edu (W. Klopper).

virtual block of the MP2 ground-state density matrix (abbreviated “MP2 density matrix” throughout the present work),

$$D_{ab}^{\text{MP2}} = \sum_{ijc} D_{ij,abc}^{\text{MP2,kern}}, \quad (1)$$

with large occupation numbers yield a large fraction of the correlation energy [7]. The kernel is given as

$$D_{ij,abc}^{\text{MP2,kern}} = \frac{2(ia|g_{12}|jc) - (ic|g_{12}|ja)}{\epsilon_{ac} - \epsilon_{ij}} \cdot \frac{2(ib|g_{12}|jc)}{\epsilon_{bc} - \epsilon_{ij}}. \quad (2)$$

Here, g_{12} denotes the Coulomb operator and ϵ_{pq} is the sum of orbital energies ϵ of orbitals p and q , respectively. In order to reduce the scaling, it has also been proposed to use the diagonal contributions only [16],

$$D_{ab}^{\text{d-MP2}} = \sum_{ic} D_{ii,abc}^{\text{MP2,kern}}, \quad (3)$$

but, after observing a significant deterioration in accuracy, the full MP2 density matrix is used throughout the present work.

2.2. Excited-state density

In the following, we discuss three main approaches, where for all schemes it is assumed that the CIS excitation vectors $\mathbf{R}^{(1)} \dots \mathbf{R}^{(n_{\text{exc}})}$ for the lowest n_{exc} excitations in the full virtual space are available if needed.

1. **(Augmented) RVS:** Use the RVS approximation as proposed by Send et al. [22] and include additionally the natural virtual orbitals (NVOs) obtained from a diagonalization of the full MP2 density matrix,

$$\mathbf{X}_{\text{MP2}}^T \mathbf{D}^{\text{MP2}} \mathbf{X}_{\text{MP2}} = \mathbf{d}, \quad (4)$$

where \mathbf{d} is a diagonal matrix containing the eigenvalues and \mathbf{X}_{MP2} are the eigenvectors. From the full set (\mathbf{X}_{MP2}) those eigenvectors (\mathbf{Y}_{MP2}) are collected that belong to eigenvalues above a given threshold, while eigenvectors belonging to an eigenvalue below the threshold are removed. Finally, the two sets are joined and linear dependencies are removed.

2. **Natural effective-density based orbitals (NEO):** Using the ground-state MP2 density and an effective excited-state(s) density,

$$D_{ab}^{\text{ex}} = \sum_{n=1}^{n_{\text{exc}}} \sum_i R_{ai}^{(n)} R_{bi}^{(n)}, \quad (5)$$

an effective density matrix is constructed using appropriate weights:

$$\mathbf{D}^{\text{eff}} = w^{(\text{MP2})} \mathbf{D}^{\text{MP2}} + w^{(\text{ex})} \mathbf{D}^{\text{ex}}. \quad (6)$$

In the present work, the weights $w^{(\text{MP2})}$ and $w^{(\text{ex})}$ were empirically chosen to be 1. The effective density matrix \mathbf{D}^{eff} is then diagonalized,

$$\mathbf{X}^T \mathbf{D}^{\text{eff}} \mathbf{X} = \mathbf{d}, \quad (7)$$

where \mathbf{d} is a diagonal matrix containing the eigenvalues and \mathbf{X} are the eigenvectors. From the full set (\mathbf{X}) those eigenvectors (\mathbf{Y}) are collected that belong to eigenvalues above a given threshold, while eigenvectors belonging to an eigenvalue below the threshold are removed.

3. **Natural transition orbitals (NTOs):** A singular value decomposition (SVD) is applied to each of the lowest n_{exc} CIS excitation vectors,

$$\mathbf{R}^{(n)} = \mathbf{U}^{(n)} \Sigma^{(n)} \mathbf{V}^{(n)T}, \quad (8)$$

and from the full set those vectors are collected that belong to singular values above a given threshold, while singular values belonging to a singular value below the threshold are removed. Note that an upper bound of the rank of the matrix $\mathbf{R}^{(n)}$ is given by $\min(n_{\text{vir}}, n_{\text{occ}})$, that is, the minimum value of the number of virtual and (active) occupied orbitals. To give an example, for the helium atom only one particle NTO can be obtained, independent of the size of the basis. These excited-state NTOs are combined with a set of NVOs based on the MP2 density matrix,

$$\mathbf{X} = \mathbf{X}_{\text{MP2}} \oplus \mathbf{V}^{(1)} \oplus \mathbf{V}^{(2)} \oplus \dots \oplus \mathbf{V}^{(n_{\text{exc}})}. \quad (9)$$

For this set of orbitals the overlap $\tilde{\mathbf{S}}$ is calculated and linear dependencies are removed using SVD,

$$\mathbf{X}^T \mathbf{X} = \tilde{\mathbf{S}} = \tilde{\mathbf{U}} \tilde{\Sigma} \tilde{\mathbf{V}}^T, \quad (10)$$

by deleting those vectors from $\tilde{\mathbf{V}}$ which belong to singular values smaller than a fixed threshold of 10^{-8} to avoid numerical instabilities, which yields the rectangular matrix $\tilde{\tilde{\mathbf{V}}}$ together with an appropriate eigenvalue matrix $\tilde{\tilde{\Sigma}}$. A linear-independent set of vectors is then obtained as

$$\mathbf{Y} = \mathbf{X} \tilde{\tilde{\mathbf{V}}} \tilde{\tilde{\Sigma}}^{1/2}. \quad (11)$$

Finally, the orbitals obtained from the three schemes are rotated such that they diagonalize the virtual-virtual block of the Fock matrix, so that they can be used in a standard coupled-cluster implementation assuming canonical orbitals provided that virtual orbitals can be frozen, *i.e.*, omitted.

3. Results

The proposed schemes have been implemented in the KOALA program package [26]. For all methods, the resolution-of-identity (RI) is used. First, the MP2-based NVOs are applied to the calculation of different ground-state correlation schemes to illustrate their broad applicability and to validate our implementation. Second, CC2 excitation energies and oscillator strengths are investigated using the new orbitals. All quantum-chemical methods used in the following are well-known in the literature, in the present work only the performance of the natural orbitals as proposed is assessed.

3.1. Ground-state correlation energies

We begin with investigating the performance of NVOs for frozen-core RI-MP2 and RI-CCSD correlation energies calculated for the water molecule using the cc-pVXZ-F12 ($X = \text{D, T, Q}$) basis sets [27], see Table 1. The table shows that already small subsets can yield large fractions of the correlation energy. For example, for the cc-pVQZ-F12 basis a threshold of 1×10^{-4} yields 40 natural virtual orbitals, which corresponds to 27%, providing 94% (95%) of the MP2 (CCSD) correlation energy, which is similar to earlier work [7]. A striking efficiency of the MP2 NVOs is observed when the explicitly-correlated RI-MP2-F12/3B-*sp* method [28] is used. For MP2 the conventional convergence with respect to the basis is observed while for MP2-F12/3B-*sp* quasi-converged results are obtained for the double-zeta basis using the MP2 NVOs. For example, the result obtained in the cc-pVDZ-F12 basis employing NVOs with a threshold of 5×10^{-4} (17 virtual orbitals) corresponds to > 96% of the best value computed in the cc-pVQZ-F12 basis without truncation of the virtual space (150 virtual orbitals). This is rooted in the large redundancy of the conventional and the explicitly-correlated double excitations [29]. One comment on

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