Use of Density Functional Theory Orbitals in the GVVPT2 Variant of Second-Order Multistate Multireference Perturbation Theory

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ABSTRACT: A new variation of the second-order generalized van Vleck perturbation theory (GVVPT2) for molecular electronic structure is suggested. In contrast to the established procedure, in which CASSCF or MCSCF orbitals are first obtained and subsequently used to define a many-electron model (or reference) space, the use of an orbital space obtained from the local density approximation (LDA) variant of density functional theory is considered. Through a final, noniterative diagonalization of an average Fock matrix within orbital subspaces, quasicanonical orbitals that are otherwise indistinguishable from quasicanonical orbitals obtained from a CASSCF or MCSCF calculation are obtained. Consequently, all advantages of the GVVPT2 method are retained, including use of macroconfigurations to define incomplete active spaces and rigorous avoidance of intruder states. The suggested variant is vetted on three well-known model problems: the symmetric stretching of the O–H bonds in water, the dissociation of N₂ and the stretching of ground and excited states C₂ to more than twice the equilibrium bond length of the ground state. It is observed that the LDA-based GVVPT2 calculations yield good results, of comparable quality to conventional CASSCF-based calculations. This is true even for the C₂ model problem, in which the orbital space for each state was defined by the LDA orbitals. These results suggest that GVVPT2 can be applied to much larger problems than previously accessible.

I. INTRODUCTION

The description of electronic structure in molecules in which both dynamic correlation and nondynamic (or static) correlation are significant remains a subject in quantum chemistry that continues to see active development. In recent years, significant advances have been made in the frameworks of multireference perturbation theory (MRPT), especially in low orders (see refs 1 and 2 for recent comparative studies) and multireference configuration-interaction (MRCI) theory, including methods with size-extensivity corrections such as the coupled electron-pair approximation (CEPA) (see ref 3 for a recent review). There have also been substantial theoretical advances in multireference coupled-cluster (MRCC) theory, although fully general computational realizations remain elusive (see refs 4 and 5 for recent reviews). Each of these frameworks has particular challenges, in addition to some shared issues.

MRPT methods are particularly challenged by the sizes of the reference (or model) spaces. Precisely because perturbation theories are most effective in low-order (e.g., consider the utility of single-reference CCSD(T) with only the triples treated perturbatively vis-à-vis MP4 theory with singles, doubles, and triples treated perturbatively; see the discussion in Chapter 14 of the monograph ref 6), a significant amount of the correlation energy in a multireference approach needs to be captured in the part of the method that is (pseudo)variational. In contrast, MRCI and MRCC theories tend to have more modest model spaces and rely more heavily on the corrections. The necessity of MRPTs (or quasi-degenerate perturbation theory (QDPTs), and we will not quibble about distinctions, real or otherwise) to use large model spaces then translates into a large number of one-electron molecular orbitals (MOs) with variable occupancies in the model space (i.e., be considered as active).

In most MRPT implementations, the model space is of the complete variety—in other words, the configurational structure generated by the active orbitals is fully variational (i.e., full configuration-interaction (FCI) theory). Generally, this approach is referred to as complete-active-space configuration-interaction (CASSCI) theory, and with the usual concomitant optimization of orbitals it is called complete-active-space self-consistent-field (CASSCF) theory. Of course, the number of variational parameters to be optimized in a CASSCF calculation grows exponentially (more precisely, doubly exponentially) with the number of orbitals. Despite the relatively simple structures of FCI wave functions, and significant theoretical and computational advances, calculations with large CASSCF spaces remain problematic (see, e.g., ref 6) and often are the limiting steps of use of MRPTs.

Use of incomplete model spaces in MRPTs is one solution, although this is not without its own problems. In contrast to...
the cost of CASSCF and CASCI calculations, the cost of general multiconfiguration self-consistent-field (MCSCF) calculations has polynomial growth with the number of orbitals. However, the number of active orbitals remains large, so that the intruder-state problem still needs attention. Also, control of size-extensivity errors becomes more difficult and, more generally, there is a significant burden on the user to be “expert.” Moreover, convergence of general MCSCF wave functions is significantly more difficult than that of CASSCF wave functions. Whereas first-order methods are usually sufficient to converge a CASSCF wave function, general MCSCF wave functions require second-order methods or advanced first-order methods that employ whole or partial spectral decompositions. Finally, whereas CASSCF wave functions have sufficiently simple structures to readily allow the use of internal contractions for the perturbation corrections, general MCSCF wave functions tend to have structures that do not allow this simplification—instead, efficient perturbation treatments must be made with elaborate layers of screening such as the use of macroconfigurations.

For both complete and incomplete model spaces, generation of MOs in which the many-electron functions (determinants or configuration-state functions (CSFs)) are expanded can become the computationally limiting step of MRPT calculations. Few alternatives have been suggested, and fewer yet have been shown to lead to practicable MRPT treatments. One of the most successful schemes is the improved orbital scheme of Chaudhuri, Freed, and co-workers, which uses a constrained Fock operator to generate the low occupancy orbitals and follows from the long-term developments of Freed and co-workers to use a sequence of Fock operators. Connections to earlier work by Huzinaga and by Morokuma and Iwata can be seen. The method has been used successfully in the context of the effective valence-shell Hamiltonian variant of MRPT and in the state-specific MRPT (SS-MRPT) of Mukherjee and co-workers. A philosophical concern with this approach is the arbitrariness of the orbital from which an electron is removed to generate the Fock operator used to construct low occupancy orbitals. Practitioners of this approach have developed robust rules for its implementation, and it does not seem to be a practical problem, at least for ground states. More recently, the emergence of so-called spin-flip methods, in which MOs are determined from a high-spin, single-determinant Hartree–Fock (HF) calculation, have been shown to be effective in a variety of post-HF methods, including MRPTs. The concern in this case is the ability to identify a globally relevant single determinant HF wave function.

In this paper, we suggest and explore an alternative protocol for obtaining MOs for MRPT calculations. Besides removing the onus of selecting a special orbital among the high-occupancy orbitals, the suggested approach has a natural connection with orbitals obtained from CASSCF calculations. Recall that CASSCF orbitals are determined for use in describing some amount electron correlation, although the variation in that “amount” with geometry can itself be problematic. We suggest that the span of the active orbitals be obtained as MOs from Kohn–Sham density functional theory (DFT) in the local-density approximation (LDA). Such MOs are simple to obtain and unambiguous. Suitability with nuclear geometrical variation is not a principal concern as the MRPT of focus for this initial study is the second-order generalized van Vleck perturbation theory (GVVPT2), which is rigorously continuous (actually differentiable) and has been shown to compensate for variations in accuracies of model spaces with geometry.

In the present study, we explore the use of LDA MOs in GVVPT2, restricting ourselves to CASCI model spaces, although extension to incomplete model spaces should be possible. After we provide a description of the method in section II, several well-known model problems are considered numerically in section III. Section IV summarizes the work.

II. METHODOLOGY

The GVVPT2 method is a subspace-specific MRPT, in which the perturbed reference functions are allowed to interact with the unperturbed functions complementary to the unperturbed reference functions in the domain of the model space. In the language of intermediate Hamiltonians, the perturbed primary functions and the unperturbed secondary functions form a basis of the effective Hamiltonian,

\[
H_{sp}^{\text{eff}} = H_{sp} + \frac{1}{2} (H_{pq} X_{qp} + X_{qp}^* H_{pq}) \quad \text{(a)}
\]

\[
H_{SS}^{\text{eff}} = H_{SS} \quad \text{(b)}
\]

where \(X_{qp}\) is the matrix representation of the first-order wave function. \(P\) is the subspace of primary functions, \(p \in P; S\) denotes the complement of \(P\) in a subspace spanned by the determinants or CSFs that form a basis of the model space, \(M\), i.e., \(P \oplus S = M\); and \(Q\) is the complement of \(M\) in the full Hilbert space. Because the electronic Hamiltonian is composed of only rank-one and rank-two excitation operators, the many-electron functions that form a basis for \(Q; q \in Q\), can be restricted for the purpose of expressing the first-order wave function, without approximation, to those functions that are no more than doubly excited relative to any function in \(M\). An element of the matrix \(X_{qp}\) has the explicit form

\[
X_{qp} = \tanh(\tilde{H}_{pq}^{(0)} - E_p^{(0)}) \frac{H_{pq}}{E_p^{(0)} - \tilde{H}_{pq}^{(0)}} \quad \text{(2)}
\]

where the superscript 0 signifies that the quantities are unperturbed. The somewhat complicated form of the coefficients of the first-order wave function ensures rigorous continuity and preservation of sensible limits. The GVVPT2 has been described in detail in previous publications, only salient features relevant to this study as described here.

The model space from which the primary functions are constructed is spanned by a basis of antisymmetrized many-electron functions (determinants or CSFs) generated from sums of products of one-electron functions obtained from a preceding calculation. The preceding calculation is in fact arbitrary, although the choice made in all preceding descriptions of the method has been a CASSCF or general MCSCF calculation. In this work, the characteristics of GVPT2 calculations constructed using MOs derived from a preceding Kohn–Sham calculation are investigated. As is well-known, the effective potential is the same for all orbitals (occupied or virtual) in Kohn–Sham theory, whereas, in Hartree–Fock theory, the potential is different for different orbitals. In particular, whereas an electron in an occupied Hartree–Fock orbital experiences the mean field generated by the other \(N - 1\) electrons in the system, an electron in a virtual Hartree–Fock orbital experiences the mean field generated by
all \( N \) electrons in the system. Consequently, Hartree–Fock virtual orbitals are more diffuse than Kohn–Sham orbitals and less suited to describe correlation. For a discussion of the suitability of Kohn–Sham orbitals for perturbation and CI treatments, see Gritsenko, Schipper, and Baerends.\textsuperscript{28,29}

Over the years, many approximate exchange–correlation functionals have been developed for Kohn–Sham calculations.\textsuperscript{30,31} In the simplest local-density approximation (LDA), the exchange–correlation functional is obtained by applying locally relations that are valid globally for the uniform electron gas.\textsuperscript{24,25,30} The LDA model provides a surprisingly good description of molecular electronic systems. In particular, its exchange–correlation hole remains localized upon dissociation of \( \text{H}_2 \) suggesting that the LDA model provides a balanced treatment of exchange and static correlation, which is important for dissociation. In the generalized gradient approximation (GGA), where density-gradient corrections are introduced in the exchange–correlation functional, thermochemistry and molecular equilibrium properties are typically better described than with LDA. On the other hand, GGA calculations are more strongly affected by triplet instabilities than are the LDA calculations. This is even truer for hybrid DFT, where some proportion of exact (orbital-dependent) DFT is introduced in the description, thereby destroying a favorable error cancellation between the description of exchange and correlation in pure DFT.\textsuperscript{28,32,33} For this reason, all calculations performed here use the simplest and most robust LDA functional.

### III. RESULTS AND DISCUSSION

Two sets of calculations were performed. In the first set, an LDA Kohn–Sham calculation was carried out to generate an orbital basis of the occupied valence orbitals and the lowest lying unoccupied orbitals, consistent with the irreducible representations generated by the atomic valence orbitals (i.e., the 2s and 2p subshells of nitrogen in dinitrogen, \( N_2 \), generate 4 \( \alpha_1 \), 2 \( \beta_1 \), and 2 \( \beta_2 \) orbitals in \( C_{2v} \) symmetry). Then, a CASCI calculation was performed in this space and the average Fock matrix constructed and diagonalized. Quasicanonical orbitals and orbital energies were obtained as eigenvectors of the rotationally invariant blocks of the average Fock matrix. GVVPT2 calculations were performed using model and external spaces spanned by antisymmetrized many-electron functions constructed from these final orbitals. In the second set of calculations, a CASSCF wave function of the same specification as the CASCI wave function described above was obtained, followed by the identical procedure for determining final orbitals and subsequent GVVPT2 calculation.

Calculations were performed using the UNDMOL suite of molecular electronic structure programs.\textsuperscript{34} The current codes cannot make use of non-Abelian point groups, so that full use of \( D_{\infty h} \) was not possible for \( C_2 \) and \( N_2 \). To allow for spin polarization of the LDA orbitals in the \( N_2 \) study, the \( C_{2z} \) subgroup of \( D_{\infty h} \) was used. In all correlated calculations based on LDA orbitals, the spatial parts of the alpha spin–orbitals were used as MOs.

#### III.A. Symmetrically Stretched Water

Description of the symmetric stretch of the two O–H bonds in water has been a staple for the assessment of new methodology, especially since the pioneering FCI results of Handy and co-workers using a DZ basis.\textsuperscript{5,36} More recent comparisons tend to use the (all-electron) FCI/cc-pVQZ results, which also consider a greater geometric variation (i.e., including 2.5 \( R_e \) and 3.0 \( R_e \) to results at 1.0, 1.5, and 2.0 \( R_e \)).\textsuperscript{37} In this study, comparison is made with results obtained in the cc-pVDZ basis.\textsuperscript{38}

The symmetric stretch of O–H bonds in water is principally of interest because of the strong variation in the amount of nondynamical correlation: near equilibrium geometries, the wave function is heavily dominated by a single determinant, whereas at the longer bond lengths, the wave function is profoundly multiconfigurational. Contrarily, the dynamic correlation is larger at the equilibrium geometry, because of the limited extent of the electron distribution function. Consequently, the ability of a method to balance the increasing nondynamical correlation with bond length with the decreasing dynamic correlation is tested.

A valence orbital space is used to construct the model space. Specifically, the eight valence electrons were distributed over the orbitals dominated by the 2s and 2p orbitals of oxygen and the 1s orbitals of hydrogen; this resulted in a valence orbital space of 3 \( \alpha_1 \), 1 \( \beta_1 \), and 1 \( \beta_2 \) MOs. All CSFs that transformed as \( 1A_1 \) defined the model space. The O(1s)-dominated lowest-energy orbital was kept doubly occupied in construction of the model space but had variable occupancy in the GVVPT2 calculation.

The agreement of GVVPT2 energies, whether based on CASSCF orbitals or on LDA orbitals, is sufficiently close to FCI results that a plot is not revealing. Instead, Figure 1 presents the difference between the GVPT2 and FCI results. As can be seen, the variation in geometry is quite small, GVPT2(CAS) values varying between about 11 and 5 mH and the GVPT2(LDA) results varying between about 7 and 3 mH. More precisely, the nonparallelity error (NPE) (i.e., the difference between the maximum deviation and minimum deviation) is 6.0 mH for the GVPT2(CAS) calculation and 3.7 mH for the GVPT2(LDA) calculation. Moreover, neither curve showed sharp or irregular features. The GVPT2(LDA) curve lies below the GVPT2(CAS) curve and is closer to the FCI curve; however, this is not a general feature of the GVPT2(LDA) model as the situation is the reversed for \( N_2 \) in a larger basis, as discussed in the next subsection.

#### III.B. Dinitrogen

The dissociation curve of the ground state of dinitrogen, \( N_2 \), is problematic for a number of methods,
primarily because of the strong interbond correlation, with concerted motion of at least three electrons. Consequently, the CCSD method fails and, perhaps not surprisingly, so does the CCSD(T) method. In contrast, even rather modest multi-configurational methods obtain qualitatively correct answers. Thus, the dinitrogen model problem is of interest partly because the MOs are not obtained with the benefit of self-consistency, thus putting the onus of orbital relaxation on GVVPT2. This model problem is also of interest because a relatively large, flexible basis set, namely, the aug-cc-pVTZ basis, has been used. Precisely because of the diffuse basis functions, the lowest lying unoccupied orbitals of a Hartree–Fock calculation would be entirely unsuitable to describe correlation. Indeed, practical experience shows that such orbitals have sufficiently small overlaps with the final correlating orbitals that they are not even good starting orbitals for CASSCF calculations. Consequently, the ability of the Kohn–Sham LDA method to obtain good low occupancy orbitals lying above the usual occupied orbitals is tested here.

Calculations were performed at 44 bond lengths, with higher density near the experimental equilibrium geometry \( R_e = 1.0975131 \text{ Å} \). The CAS model space was generated by distributing the 10 valence electrons among the 8 valence orbitals, in all ways consistent with a spin singlet and the \( \Sigma^{-} \) irrep of the \( C_{2v} \) point group. The 1s-dominated orbitals were held doubly occupied in all calculations.

There are six potential energy curves in Figure 2, calculated with the LDA method, with the CASSCF method and the MRCISD method in the same CAS space, with the CASCI method using LDA orbitals, and with the GVVPT2(LDA) and GVVPT2(CAS) methods. The energy curves are virtually identical near the equilibrium distance, staying close to one another as the distance increases to about 1.7–1.8 Å. At that distance, which corresponds to the beginning of the transition to atomic-like orbitals, the curves gradually spread until the onset of the asymptotic region near 2.3 Å. It is interesting that the CASSCF, CASCI, and GVVPT2(CAS) curves have asymptotes that cluster around 0.33–0.34 H, whereas the GVVPT2(LDA) asymptote at 0.36 H is a little higher. It can be seen that, although the GVVPT2(CAS) curve is parallel to the MRCISD curve at essentially all bond lengths (including the difficult crossover region, see insert), the GVVPT2(LDA) curve, though still satisfactory, deviates somewhat more at longer bond lengths. The MRCISD dissociation energy at 0.348 H lies between the two values, but slightly closer to the GVVPT2(CAS) limit of 0.341 H than to the GVVPT2(LDA) limit of 0.360 H. It is tempting to speculate that the higher energy of the GVVPT2(LDA) method relative to the GVVPT2(CAS) method is related to the performance of the LDA method itself, which greatly overestimates the energy in the dissociation limit; see ref 38. However, we also note that the MRCISD energy is not size extensive and that a size-extensivity correction would increase the MRCISD dissociation energy, making it difficult to draw firm conclusions regarding the relative performance of the GVVPT2(LDA) and GVVPT2(CAS) methods.

### III.C. Dicarbon.

The ground and two lowest-lying excited spin-singlet states of \( C_2 \) are problematic because of the strong geometry-dependent proximities of curves, which undergo an avoided crossing between \( 1^\Sigma_g^+ \) and \( 2^\Sigma_g^- \), an actual crossing between \( 1^\Sigma_g^{-} \) and \( 1^\Delta_g \) within the interval of 1.5–2.0 Å and a crossing between \( 2^\Sigma_g^{-} \) and \( 1^\Delta_g \) at a shorter bond length; see Figure 3. The FCI calculations of Abrams and Sherrill, using a

![Figure 2. Potential energy curves of the ground state of N₂ as a function of internuclear distance (Å) relative to the minimum energy of a particular method: LDA results in gray; CASSCF in orange; CASSCF in dark cyan; GVVPT2, based on CASSCF orbitals, in red; GVVPT2 based on LDA orbitals in blue; MRCISD in black. The inset shows an expanded view near the crossover from molecular to atomic regimes.](image)

![Figure 3. Potential energy curves of the 1,2\(^1\Sigma_g^+\) (black and blue, respectively) and 1\(^1\Delta_g\) (red) states of C₂. Solid lines are Bézier interpolations of data from ref 42; points are results of GVVPT2(LDA) calculations.](image)
particle reduced density matrix with a (1:1:1) weighting of density matrices from CI calculations in the space of model space LDA orbitals.

As can be seen from Figure 3, the GVVPT2(LDA) results for the $1\Sigma_g^+$ state (black triangles) are close to the FCI results (shown as a continuous black curve). Indeed, the largest deviation is only 22 mH, and the NPE over the considered abscissae is 7 mH. Furthermore, and perhaps more interesting, is the close agreement of the GVVPT2(LDA) curves for the $2\Sigma_u^+$ and $1\Delta_g$ states and the FCI curves, using an orbital space from ground-state LDA calculations. For $2\Sigma_u^+$, the maximum deviation from the FCI curve is slightly larger than 22 mH and the NPE is 8 mH; similarly, the maximum deviation for the $1\Delta_g$ state is 22 mH, whereas the NPE is here only 3 mH. Consequently, the GVVPT2(LDA) curves are well behaved in the crossing and avoided crossing regions.

IV. CONCLUSIONS

The use of MOs derived from Kohn–Sham LDA calculations for use in GVVPT2 calculations has been suggested and demonstrated to be efficacious for three widely studied representative problems. Each of the three model problems, the symmetric stretching of the O−H bond in H$_2$O, the dissociation curve of N$_2$ and the stretching of the bond in C$_2$, is more strongly varying amounts of quasidegeneracy (with geometry), so that the usual GVVPT2 paradigm of nondynamic correlation being treated by the underlying MCSCF expansion is clearly challenged. In the case of the H$_2$O molecule, the problem, which uses a cc-pVDZ basis, the maximum error difference is 7.1 mH, with an NPE of 3.4 mH. Moreover, the difference curves are very smooth. The GVVPT2 relative energy curves for N$_2$, using an aug-cc-pVTZ basis, based on an LDA orbital space resulted in an NPE of 18.6 mH (relative to best available results, which was MRCCSD results based on CASSCF orbitals). It is noteworthy that the presence of diffuse basis functions does not invalidate the suggested protocol, although it should be noted that the unoccupied LDA orbitals in N$_2$ were still of valence character. The performance of the suggested protocol when yet larger basis sets are used, and specifically when the unoccupied orbitals acquire greater Rydberg character, remains to be tested. In many ways, the most remarkable result was for the C$_2$ molecule, with DZP basis. It was shown that GVVPT2 based on LDA orbitals for the ground state was able to describe not only the $1\Sigma_g^+$ ground state (8 mH NPE) but also the $2\Sigma_u^+$ and $1\Delta_g$ excited states (8 and 3 mH NPE, respectively).

The use of ground-state LDA orbital spaces for subsequent GVVPT2 calculations appears to be robust for situations in which the LDA Kohn–Sham method itself is not expected to be accurate. This study extends the usefulness of GVVPT2, because the potentially time-consuming (and arguably user biased) optimization of MOs in a preceding CASSCF (or MCSCF) step appears unnecessary. As a result, we expect that larger molecules will become accessible to GVVPT2. One may also suspect that LDA orbital spaces would provide efficacious support not only for GVVPT2 (and MRCCSD) but also for other effective Hamiltonian methods.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Norwegian Research Council through the CoE Centre for Theoretical and Computational Chemistry (CTCC) Grant Nos. 179568/V30 and 171185/V30 and through the European Research Council under the European Union Seventh Framework Program through the Advanced Grant ABACUS, ERC Grant Agreement No. 267683. M.R.H. is grateful to the NSF (Grant No. EPS-0814442) for additional support.

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