

New perspectives in multireference perturbation theory: the n -electron valence state approach

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Abstract The n -electron valence state perturbation theory (NEVPT) is a form of multireference perturbation theory which is based on a zero order reference wavefunction of CAS-CI type (complete active space configuration interaction) and which is characterized by the utilization of correction functions (zero order wavefunctions external to the CAS) of multireference nature, obtained through the diagonalization of a suitable two-electron model Hamiltonian (Dyall's Hamiltonian) in some well defined determinant spaces. A review of the NEVPT approach is presented, starting from the original second order state-specific formulation, going through the quasidegenerate multi-state extension and arriving at the recent implementations of the third order in the energy and of the internally contracted configuration interaction. The chief properties of NEVPT—size consistence and absence of intruder states—are analyzed. Finally, an application concerning the calculation of the vertical spectrum of the biologically important free base porphyrin molecule, is presented.

Keywords Multireference perturbation theory · NEVPT · Internally contracted CI · Free base porphyrin

1 Introduction

Multireference perturbation theories (MRPT) play an important rôle in the treatment of electronic correlation in molecules. In many molecular phenomena such as the breaking of a chemical bond or the electronic transition

to an excited state, a single reference wavefunction does not suffice to provide a reasonable approximation to the solution of the time independent Schrödinger equation; many electronic configurations can be important and a zero order description of the electronic structure of the molecule may not leave out of consideration such quasidegenerate configurations. The inclusion of the quasidegenerate configurations accounts for what is called the static (or non-dynamical) correlation; the rest of the correlation energy (the dynamical component) could be dealt with perturbationally with a suitable MRPT which should, hopefully, be as efficient as the Møller–Plesset PT [1] in the case of a single reference Hartree–Fock wavefunction. A major issue in MRPT concerns the definition of a proper zero order Hamiltonian H_0 . In the early theories, which were developed at the beginning of the 1970s, such as CIPSI [2], H_0 was defined in terms of a one-electron, Fock-like, operator and the zero order functions (referred to as correction functions or, more succinctly, as perturbers) used to build the first order correction to the wavefunction, were simple Slater determinants. The idea that H_0 should be based on a one-electron operator is still dominant in most modern MRPTs. For instance in CASPT2 [3,4], one of the most successful forms of MRPT, H_0 is a projected generalized Fock operator and the perturbers are built in terms of internally contracted excitations (*vide infra*). Dyall [5] showed that the usage of correction functions deriving from a one-electron operator introduces a bias in the energy calculation since the zero order reference wavefunction properly takes into consideration the bielectronic interactions occurring among the active electrons whereas the correction functions are not allowed to do so. In order to obviate such difficulty Dyall introduces a model Hamiltonian, partly bielectronic in

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character, which acts as H_0 . In 2001, based on Dyal's work, the “ n -electron valence state perturbation theory” (NEVPT) was put forward [6], in collaboration between the theoretical chemistry groups of the universities of Ferrara and Toulouse. NEVPT is based on a zero order variational wavefunction of Complete Active Space Configuration Interaction (CAS-CI) type and on correction functions still of multireference type where the bielectronic interactions among active electrons are properly considered. Different formulations of NEVPT are possible according to the type of Hamiltonian employed for the definition of H_0 and according to the degree of contraction of the perturbers.

The following sections are devoted to a review of the developments that have concerned NEVPT during the last five years. In order to show the applicability of NEVPT, the last section will report calculations, expressly prepared for this article, on the theoretical description of the vertical spectrum of the free base porphyrin molecule.

2 The second order NEVPT approach

2.1 The first order interacting space

NEVPT is based on a reference variational wavefunction of CAS-CI (usually CASSCF) type. The molecular orbitals can consequently be divided into three classes: core orbitals with occupation number always equal to 2 in all the determinants of the CAS, active orbitals with all possible occupation numbers and virtual orbitals, never occupied. The core, active and virtual orbitals will be denoted, respectively, with indices i, j, \dots, a, b, \dots , and r, s, \dots , (generic orbitals will have indices w, x, \dots).

The first order interacting space [7], S , is defined as the vector space spanned by all the determinants, external to the CAS, which have nonvanishing interaction with the zero order multireference wavefunction $\Psi_m^{(0)}$. S can be envisaged as the direct sum of subspaces $S_l^{(k)}$ spanned by determinants which share the same pattern l of core and virtual orbitals (referred to collectively as *inactive* orbitals) and the same number k of electrons added to (or removed from) the active space. There are only eight typologies of $S_l^{(k)}$ subspaces: $S_{ij,rs}^{(0)}$ with two core orbitals substituted by two virtuals, $S_{i,r}^{(0)}$ with one core orbital substituted by one virtual, $S_{ij,r}^{(+1)}$ with one core substituted by one virtual and one core electron added to the active space, $S_i^{(+1)}$ with one core electron added to the active space, $S_{i,rs}^{(-1)}$ with one core orbital substituted by one virtual and one active electron excited into a virtual, $S_r^{(-1)}$ with one active electron excited into a virtual, $S_{ij}^{(+2)}$

with two core electrons excited to the active space, $S_{rs}^{(-2)}$ with two active electrons excited to the virtual space.

The usage of such subspaces with their full dimensionality leads to the “totally uncontracted” NEVPT2. The zero order correction functions could in principle be obtained by diagonalizing the electronic Hamiltonian within each subspace $S_l^{(k)}$: $P_{S_l^{(k)}} H P_{S_l^{(k)}} \Psi_{l,\mu}^{(k)} = E_{l,\mu}^{(k)} \Psi_{l,\mu}^{(k)}$. Such a choice, anyway, appears as computationally very expensive, requiring a CAS-CI calculation for each occurrence of the $S_l^{(k)}$ subspaces. A more viable approach within the totally uncontracted scheme would consist in building up the correction functions $\Psi_{l,\mu}^{(k)}$ with a model Hamiltonian, simplified with respect to the true H , but still able to take into account the bielectronic interactions among the active electrons. A good model Hamiltonian has been provided by Dyal in an important paper in 1995 [5]; the form of Dyal's Hamiltonian is the following:

$$H^D = H_i + H_v + C, \quad (1)$$

where H_i is a one-electron operator defined in terms of orbital energies and creation/destruction pairs

$$H_i = \sum_i^{\text{core}} \epsilon_i E_{ii} + \sum_r^{\text{virt}} \epsilon_r E_{rr}, \quad (2)$$

H_v is a two-electron operator confined to the active orbital space

$$H_v = \sum_{ab}^{\text{act}} h_{ab}^{\text{eff}} E_{ab} + \frac{1}{2} \sum_{abcd}^{\text{act}} \langle ab|cd \rangle (E_{ac} E_{bd} - \delta_{bc} E_{ad}), \quad (3)$$

and C is a suitable constant assuring that H^D is equivalent to H within the CAS space ($C = 2 \sum_i^{\text{core}} h_{ii} + \sum_{ij}^{\text{core}} (2 \langle ij|ij \rangle - \langle ij|ji \rangle) - 2 \sum_i^{\text{core}} \epsilon_i$). In the above formulas use has been made of the spin-traced excitation operators [8] $E_{wx} = a_{w\alpha}^+ a_{x\alpha} + a_{w\beta}^+ a_{x\beta}$. The quantities h_{ab}^{eff} appearing in Eq. 3 are the usual one-electron matrix elements h_{ab} supplemented with a contribution allowing for the effective field of the core electrons ($h_{ab}^{\text{eff}} = h_{ab} + \sum_j^{\text{core}} (2 \langle aj|bj \rangle - \langle aj|jb \rangle)$). The orbital energies ϵ_i and ϵ_r are usually chosen as those which result from the canonicalization of the core and virtual orbitals. The diagonalization of H^D within the $S_l^{(k)}$ subspaces is much simpler than that of H . Let us consider, as an example, the $S_{ij,r}^{(+1)}$ subspaces. The matrix elements of H^D are readily seen to be equivalent, apart from a constant shift in the diagonal, to those of H for the case of an ionized molecule with one electron added to the active space.

In other words, if $\Psi_\mu^{(+1)}$ is the CAS-CI solution to the problem $P_{\text{ion}} H P_{\text{ion}} \Psi_\mu^{(+1)} = E_\mu^{(+1)} \Psi_\mu^{(+1)}$, one has for H^D :

$$\Psi_{ijr,\mu}^{(+1)} = a_r^+ a_i a_j \Psi_\mu^{(+1)},$$

$$H^D \Psi_{ijr,\mu}^{(+1)} = \left(E_\mu^{(+1)} + \epsilon_r - \epsilon_i - \epsilon_j \right) \Psi_{ijr,\mu}^{(+1)} \quad (4)$$

Similar considerations apply to all the other typologies of subspaces $S_l^{(k)}$. The number of diagonalizations is therefore reduced to that of possible ions with charge k ($-2 \leq k \leq 2$) with all possible spin couplings and symmetry cases. The procedure above outlined is feasible for CAS of moderate size but appears impractical for dimensions above a few thousands, which is common practice in nowadays' calculations.

2.2 The internally contracted approach

The difficulties met with a totally uncontracted approach can be substantially alleviated by taking into consideration internally contracted (IC) correction functions. It has long been recognized [9,10] that if a function Φ , external to the CAS, interacts with the reference wavefunction then $\langle \Psi_m^{(0)} | H | \Phi \rangle = \langle \Psi_m^{(0)} | H | P_{\text{IC}} \Phi \rangle$ where P_{IC} projects onto the “internally contracted” first order space, spanned by all the functions $E_{wx} E_{yz} \Psi_m^{(0)}$ not belonging to the CAS. Since the second order correction to the energy can be expressed as $E_m^{(2)} = \langle \Psi_m^{(0)} | V | \Psi_m^{(1)} \rangle$, it is clear that $\Psi_m^{(1)}$ can be restricted to belong to the IC first order space. Hence, the $S_l^{(k)}$ subspaces will be now restricted to be spanned by functions of the type $E_{wx} E_{yz} \Psi_m^{(0)}$. The advantage of the IC formulation is that the dimension of a given IC $S_l^{(k)}$ is now much lower than its uncontracted analog; for instance the IC $S_{ij,r}^{(+1)}$ subspace is spanned by the functions $E_{ri} E_{aj} \Psi_m^{(0)}$, the number of which is n_{act} , the number of active orbitals. A minor disadvantage of the IC approach is that the $E_{wx} E_{yz} \Psi_m^{(0)}$ functions are not orthogonal and, generally, not even linearly independent, so that care has to be taken in removing the possible linear dependencies.

The “partially contracted” NEVPT (PC-NEVPT2) consists in building the correction functions as multireference wavefunctions belonging to the various IC $S_l^{(k)}$ subspaces. One possibility would be to diagonalize the true Hamiltonian H within each such subspace but this would be computationally too expensive. The actual choice adopted in PC-NEVPT2 has been to utilize the model Hamiltonian H^D in the diagonalization: the active part of H^D (H_v) has matrix elements within a given $S_l^{(k)}$ space which do not depend on the inactive orbital pattern l ; for instance in $S_{ij,r}^{(+1)}$ the matrix elements of H_v are

independent of the choice of the i, j and r indices. On the other hand, the inactive part H_i only produces an energy shift within $S_l^{(k)}$ ($(\epsilon_r - \epsilon_i - \epsilon_j)$ for $S_{ij,r}^{(+1)}$), hence just one single diagonalization is required to provide all the possible eigenfunctions of H^D for all the IC $S_l^{(k)}$ subspaces of a given typology. The details for the diagonalization of H^D in the various $S_l^{(k)}$ can be found in Ref. [11]. Here, we only remember that the general form of the eigenvalues is: $E_{l,\mu}^{(k)} = E_m^{(0)} + \Delta\epsilon_l + e_\mu$ where $\Delta\epsilon_l$ equals the difference of the virtual and core orbital energies involved in the definition of $S_l^{(k)}$ and where $E_m^{(0)} + e_\mu$ is the μ th eigenvalue of the projection of H_v onto the IC $S_l^{(k)}$; e_μ is independent of the inactive orbitals and represents a physical process occurring in the active space. So, in the $S_{ij,r}^{(+1)}$ subspaces, e_μ approximates an electron affinity due to an electron passing from the core to the active space, in the $S_{ij}^{(+2)}$ subspaces the eigenvalues e_μ approximate an energy of double ionization and so on for the other subspaces. The largest dimensions among the eight typologies of $S_l^{(k)}$ subspaces are those occurring for $S_i^{(+1)}$ and $S_r^{(-1)}$. $S_i^{(+1)}$ ($S_r^{(-1)}$) is spanned by the functions $E_{bi} E_{ac} \Psi_m^{(0)}$ ($E_{rb} E_{ac} \Psi_m^{(0)}$) the number of which amounts to n_{act}^3 . Such a number is an upper limit to the true dimension of the two subspaces since linear dependencies are generally present. The $S_i^{(+1)}$ and $S_r^{(-1)}$ subspaces are also the most demanding with respect to the evaluation of the matrix elements of the H_v operator since the four-particle density matrix is required. Anyway, the four-particle density matrix has indices confined to the active orbitals and its storage in the memory of the computer does not present serious difficulties provided that the dimension of the active space remains sufficiently small. At present $n_{\text{act}} = 14$ is the limit we have set in our NEVPT codes but this is also a practical limit in most CASSCF calculations. It can be remarked that the PC-NEVPT2 makes use of exactly the same functional space as CASPT2 [3, 4] does; the difference between the two approaches is that PC-NEVPT2 uses multireference correction functions $\Psi_{l,\mu}^{(k)}$ which are eigenfunctions of a simplified two-electron Hamiltonian (H^D) taking into due account the bielectronic interactions among the active electrons. The zero order Hamiltonian of PC-NEVPT can be written as follows:

$$H_0^{\text{PC}} = P_{\text{CAS}} H P_{\text{CAS}} + \sum_{l,k} P_{S_l^{(k)}} H^D P_{S_l^{(k)}} \quad (5)$$

where $P_{S_l^{(k)}}$ is the projector onto the IC $S_l^{(k)}$ defined above.

2.3 The strongly contracted NEVPT2

The NEVPT2 approach can be further simplified by requiring that a single correction function $\Psi_l^{(k)}$ be chosen from each IC $S_l^{(k)}$ subspace. $\Psi_l^{(k)}$ is chosen by the following projection:

$$\Psi_l^{(k)} = P_{S_l^{(k)}} H \Psi_m^{(0)}. \quad (6)$$

The correction functions thus obtained are orthogonal (but not normalized to one) and can be used to build a perturbation series; the energy pertaining to $\Psi_l^{(k)}$ can be defined by a Rayleigh quotient

$$E_l^{(k)} = \frac{\langle \Psi_l^{(k)} | H | \Psi_l^{(k)} \rangle}{\langle \Psi_l^{(k)} | \Psi_l^{(k)} \rangle}. \quad (7)$$

Such a formula can be further simplified by substituting the true Hamiltonian H with the model H^D . The resulting formulation has been called “strongly contracted” NEVPT (SC-NEVPT2) and is the first approach that has been practically implemented [12, 11]. It should be noticed that, despite their low number, the $\Psi_l^{(k)}$ functions can be considered to be, in a sense, complete for the construction of a second order perturbation theory; actually, it is easily verified that a given function Φ belonging to $S_l^{(k)}$ and orthogonal to $\Psi_l^{(k)}$ has no interaction with $\Psi_m^{(0)}$: $\langle \Psi_m^{(0)} | H | \Phi \rangle = 0$. The zero order Hamiltonian of SC-NEVPT can be expressed as a spectral decomposition

$$H_0^{\text{SC}} = P_{\text{CAS}} H P_{\text{CAS}} + \sum_{l,k} |\Psi_l^{(k)'}\rangle E_l^{(k)} \langle \Psi_l^{(k)'}| \quad (8)$$

where $\Psi_l^{(k)'} = \Psi_l^{(k)} / \|\Psi_l^{(k)}\|$. The second order contribution to the energy, as shown in Ref. [11], can be conveniently expressed as

$$E_m^{(2)} = \sum_{l,k} \frac{\|\Psi_l^{(k)}\|^2}{E_m^{(0)} - E_l^{(k)}}. \quad (9)$$

The detailed expressions of the norms $\|\Psi_l^{(k)}\|$ in terms of the two-electron integrals and spinless density matrices of various particle rank are reported in Ref. [11]. Despite the low number of correction functions employed, the SC-NEVPT2 usually yields results very similar to those of the more accurate PC-NEVPT2, implying that the averaging process which is inherent in the strongly contracted approach is rather effective. An interesting inequality was proved in Ref. [11], showing that, for

each $S_l^{(k)}$ subspace, the contribution to the second order correction to the energy of PC-NEVPT2 is always lower (negative and larger in absolute value) than that of SC-NEVPT2. Cases of significant discrepancies between SC- and PC-NEVPT2 are usually indicative of some defect in the zero order wavefunction $\Psi_m^{(0)}$ such as, for instance, an inaccurate selection of the active orbitals.

3 Properties of the NEVPT2 approaches

3.1 Invariance under unitary transformations of orbitals and size consistence

Each $S_l^{(k)}$ subspace is a complete active space and is therefore invariant under an arbitrary rotation of the active orbitals. Such a property remains true passing from the uncontracted definition of $S_l^{(k)}$ either to the internally contracted one or also to the one-dimensional subspaces spanned by the strongly contracted correction functions. As a consequence, the zero order Hamiltonian used in the various NEVPT2 approaches, either with the true or with the model Hamiltonian, is invariant under rotation of the active orbitals and the correction to the energy (and to the wavefunction) to any order of perturbation shares this important invariance property. As regards the behaviour of NEVPT with respect to the inactive orbitals, we notice that the form of the model Hamiltonian H^D given in Eq. 1 is clearly not invariant under rotation of the core or virtual orbitals. A simple modification guaranteeing the invariance is given by redefining the inactive part of H^D

$$H_i^D = \sum_{ij}^{\text{core}} f_{ij} E_{ij} + \sum_{rs}^{\text{virt}} f_{rs} E_{rs} \quad (10)$$

where f_{ij} and f_{rs} are elements of generalized Fock matrices

$$f_{ij} = -\langle a_i | \Psi_m^{(0)} | H | a_j | \Psi_m^{(0)} \rangle + \delta_{ij} E_m^{(0)} \quad (11)$$

$$f_{rs} = \langle a_r^+ | \Psi_m^{(0)} | H | a_s^+ | \Psi_m^{(0)} \rangle - \delta_{rs} E_m^{(0)} \quad (12)$$

If the inactive orbitals are chosen so as to diagonalize the Fock matrices (canonical orbitals), one goes back to the original definition of H^D . Sometimes it may be convenient to use noncanonical inactive orbitals, as, for instance, when working with a priori localized orbitals [13]. In such cases one can use the modified Dyllal's Hamiltonian of Eq. 10, with the following redefinition of H_0

$$H_0 = P_{\text{CAS}} H P_{\text{CAS}} + \sum_{\substack{l,k \\ l',k'}} P_{S_l^{(k)}} H^D P_{S_{l'}^{(k')}} \quad (13)$$

The coupling between different $S_l^{(k)}$ spaces is dealt with very simply because the matrix elements of H_l^D can only occur between functions of $S_l^{(k)}$ subspaces belonging to the same typology (for instance $S_{ij,r}^{(+1)}$ has matrix elements only with $S_{i',j',r}^{(+1)}$ or with $S_{ij,r}^{(+1)}$). Such noncanonical PC-NEVPT2 approach has been implemented in our laboratory by solving the perturbation equations in the form of a system of linear equations

$$\Psi_m^{(1)} = \sum_{l,k,\mu} c_{l\mu}^{(k)} \Psi_{l,\mu}^{(k)}$$

$$\sum_{l',k',\mu'} c_{l'\mu'}^{(k')} \langle \Psi_{l',\mu'}^{(k')} | H_0 - E_m^{(0)} | \Psi_{l,\mu}^{(k)} \rangle = -\langle \Psi_{l,\mu}^{(k)} | V | \Psi_m^{(0)} \rangle$$

where the $\Psi_{l,\mu}^{(k)}$ functions are obtained by a preliminary PC-NEVPT2 calculation making use of only the diagonal elements of the Fock matrices. It should be remarked that in the strongly contracted approach the zero order Hamiltonian is *not* invariant under rotation of the core or virtual orbitals; in our codes we make use of the canonical orbitals for the SC-NEVPT variant. Furthermore, it is worth remembering that NEVPT is not invariant under rotations between active and inactive orbitals and care must be devoted to a proper choice of the active space so as to avoid possible exchanges of the identities of the orbitals which might occur, for instance, following the changes of the geometrical parameters of a molecule.

A direct consequence of the above discussed invariance is that, as shown in Ref. [6], the NEVPT2 approaches based on Dyllal's Hamiltonian enjoy the valuable property of size consistence in the form of strict separability: the energy of two noninteracting systems A and B is the same whether calculated in the supermolecule approach or evaluated as the sum of the two separated systems. If the true Hamiltonian were used instead of H^D , this property would generally cease to be true in the case of a system composed of two identical parts; in order to recover the strict separability, use should be made of orbitals localized in the two fragments.

3.2 Absence of intruder states

In a perturbation theory the “intruder states” are those correction functions which have an energy (eigenvalue of H_0) close to the reference energy $E_m^{(0)}$, thus causing near divergences in the perturbation summation. The presence of intruder states is a notorious Achilles' heel in MRPT's based on a one-electron zero order

Hamiltonian: the inability in correctly describing the two-electron interactions between the correction functions affects the description of the energies of the perturbers. In the CIPSI method [2], where simple determinants are used as perturbers, a remedy against the intruder states is afforded by the usage of Epstein–Nesbet [14, 15] denominators, at the cost of a worsening of the size consistence properties. In CASPT2 a partial ad hoc solution to the intruder state problem is given by the adoption of energy shifts in the denominators [16], which are anyway difficult to justify in physical terms.

The correction functions used in NEVPT2, in all its variants, are practically exempt from the intruder state phenomenon. Taking for instance the PC-NEVPT2 with Dyllal's Hamiltonian, one has for the energy associated to $\Psi_{l,\mu}^{(k)}$

$$E_{l,\mu}^{(k)} = E_m^{(0)} + \Delta\epsilon_l^{(k)} + e_\mu \quad (14)$$

$\Delta\epsilon_l^{(k)}$ and e_μ are both positive quantities with e_μ representing the energy of a well defined physical process occurring in the active space (such as an ionization potential, an electron affinity, an electronic excitation, etc.). The subspaces which appear as more exposed to the possibility of intruder states are those of type $S_r^{(-1)}$. The energies are here $E_r^{(-1)} = E_m^{(0)} + \epsilon_r + e_\mu$. If r refers to a very diffuse orbital, its energy ϵ_r is close to zero; e_μ describes an ionization in the active space and could be very small only for a highly excited state. Thus, the possibility of being affected by intruder states appears as rather remote in PC-NEVPT2 (but similar considerations also apply to SC-NEVPT2) and, actually, we have never met with divergences in all the calculations carried out thus far.

3.3 Spin properties

The first order correction to the wavefunction $\Psi_m^{(1)}$, is expressed in terms of the $\Psi_{l,\mu}^{(k)}$ perturbers in PC-NEVPT2 ($\Psi_l^{(k)}$ in SC-NEVPT2). Such correction functions are built by the application of products of spin-traced excitation operators $E_{wx}E_{yz}$ to $\Psi_m^{(0)}$. Since the E_{wx} operators commute with the square of the total spin operator and with its projection onto the z axis, $\Psi_m^{(1)}$ is a pure spin function and has the same spin eigenvalues as $\Psi_m^{(0)}$.

3.4 Reduction to MP2

Dyllal's model Hamiltonian H^D represents a natural extension of the zero order Møller–Plesset (MP) H_0^{MP} and it coincides with H_0^{MP} in case the active space is

empty. Hence the two variants of NEVPT2 based on H^D reduce to MP2 if a Hartree–Fock determinant is chosen as zero order wavefunction. The two variants based on the true Hamiltonian would instead reduce to the Epstein–Nesbet second order PT.

4 Quasidegenerate NEVPT2

The MRPT thus far presented belongs to the so-called “diagonalize-then-perturb” approach, where the first order correction to the wavefunction brings no modification to the zero order variational reference. In some circumstances, though, the coefficients of the configurations which make up the variational wavefunction turn out to be rather poorly described, lacking important differential correlation contributions; typical cases are the avoided crossings between neutral and ionic states as well as electronically excited states of mixed valence—Rydberg character. Such cases are conveniently dealt with by the use of a quasidegenerate perturbation theory [17–20] (QDPT) where the required redefinition of the coefficients is carried out by the diagonalization of an effective Hamiltonian in a configuration space of limited dimension. A quasidegenerate formulation of NEVPT2 has been given in Ref. [21] for both the strongly and partially contracted approaches (QD-SCNEVPT2 and QD-PCNEVPT2) with use of the model Hamiltonian H^D . In the QD-NEVPT2 approach a model space is chosen by selecting as basis set a few solutions of the CAS-CI problem $\{\Psi_1^{(0)}, \Psi_2^{(0)}, \dots, \Psi_g^{(0)}\}$ with $P_{\text{CAS}}H P_{\text{CAS}}\Psi_m^{(0)} = E_m^{(0)}\Psi_m^{(0)}$. The purpose of the QDPT is to find the projections of the true eigenfunctions onto the model space with the use of an effective Hamiltonian

$$H_{\text{eff}}\tilde{\Psi}_m = E_m\tilde{\Psi}_m, \quad (15)$$

where $\tilde{\Psi}_m = P\Psi_m$, $P = \sum_{k=1}^g |\Psi_k^{(0)}\rangle\langle\Psi_k^{(0)}|$ and E_m is the true eigenvalue associated to the true eigenfunction Ψ_m . Introducing the wave operator Ω by the relation $\Omega\tilde{\Psi}_m = \Psi_m$, the effective Hamiltonian can be written as $H_{\text{eff}} = PH\Omega$ and Ω can be obtained by solving the generalized Bloch equation

$$\Omega PH\Omega - H\Omega = 0; \quad (16)$$

expanding Ω and H_{eff} in a perturbation series

$$\Omega = P + \Omega^{(1)} + \Omega^{(2)} + \dots \quad (17)$$

$$H_{\text{eff}} = H_{\text{eff}}^{(0)} + H_{\text{eff}}^{(1)} + H_{\text{eff}}^{(2)} + \dots \quad (18)$$

one obtains $[\Omega^{(1)}, H_0] = QVP$, $H_{\text{eff}}^{(0)} = PH_0P$, $H_{\text{eff}}^{(1)} = PVP = 0$, $H_{\text{eff}}^{(2)} = PV\Omega^{(1)}$. Working formulas for $\Omega^{(1)}$

and $H_{\text{eff}}^{(2)}$ can be obtained using the correction functions $\Psi_{l,\mu}^{(k)}$ (for the PC-NEVPT) or $\Psi_l^{(k)}$ (for the SC-NEVPT). Since, the two NEVPT forms are state-specific theories, with H_0 depending on a given reference wavefunction $\Psi_m^{(0)}$, a dilemma arises as to which correction functions should be used. The question is answered by Zaitsevski and Malrieu’s [22] multipartitioning technique which allows one to use different partitions of the Hamiltonian according to the various $\Psi_m^{(0)}$ functions of the model space $H = H_0(m) + V(m)$ with

$$H_0(m) = P_{\text{CAS}}H P_{\text{CAS}} + \sum_{l,k,\mu} |\Psi_{l,\mu}^{(k)}(m)\rangle E_{l,\mu}^{(k)} \langle\Psi_{l,\mu}^{(k)}(m)|, \quad (19)$$

where $\Psi_{l,\mu}^{(k)}(m)$ are the correction functions of the IC $S_l^{(k)}$ relating to the $\Psi_m^{(0)}$ reference. The matrix elements of H_{eff} up to second order are given by

$$\begin{aligned} &\langle\Psi_n^{(0)}|H_{\text{eff}}|\Psi_m^{(0)}\rangle \\ &= E_m^{(0)}\delta_{mn} + \sum_{l,k,\mu} \frac{\langle\Psi_n^{(0)}|H|\Psi_{l,\mu}^{(k)}(m)\rangle\langle\Psi_{l,\mu}^{(k)}(m)|H|\Psi_m^{(0)}\rangle}{E_m^{(0)} - E_{l,\mu}^{(k)}(m)}. \end{aligned} \quad (20)$$

The diagonalization of the nonhermitian \mathbf{H}_{eff} matrix produces the desired mixing within the model space

$$\tilde{\Psi}_m = \sum_{k=1}^g \Psi_k^{(0)} c_{km}, \quad \mathbf{H}_{\text{eff}}\mathbf{c}_m = E_m\mathbf{c}_m.$$

From a computational point of view, the matrix elements appearing in Eq. 20 require, besides the quantities employed in the single state NEVPT2, also the evaluation of the transition density matrix of particle rank not higher than three. Altogether, the QD-NEVPT2 approach requires little extra effort beyond the calculations needed in the separate g single state NEVPT2 evaluations.

5 Third order NEVPT and internally contracted CI

The first order correction to the wavefunction can be used to determine up to the third order correction to the energy

$$E_m^{(3)} = \langle\Psi_m^{(1)}|V|\Psi_m^{(1)}\rangle - E_m^{(1)}\|\Psi_m^{(1)}\|^2 \quad (21)$$

and in NEVPT the last term on the rhs of the above equation is null since $E_m^{(1)} = 0$. In the strongly and partially contracted approaches $\Psi_m^{(1)}$ is expanded on a

rather limited set of correction functions and, as was formerly shown by Werner [23] in his CASPT3 formulation, the task of building a third order algorithm can be attained without excessive computational effort. Besides its intrinsic value, a third order approach would constitute an important test to judge on the efficiency and stability of the perturbation series: too large a discrepancy between the second and third order result would be a clear clue of the inadequacy of the zero order wavefunction. In order to utilize Eq. 21 one needs the matrix elements of the true Hamiltonian between the correction functions. In the internally contracted approaches, the matrix elements of H between IC functions $E_{wx}E_{yz}\Psi_m^{(0)}$ are required. In principle, no new quantities with respect to the NEVPT2 formulations are necessary since a given matrix element, as is readily recognized, can be written in terms of density matrices of particle rank not exceeding four. The awkward task of delivering all the required matrix elements between IC functions has been entrusted to a symbolic program dubbed FRODO [24,25] (an acronym for “formal reduction of density operators”), written in the computer algebra system MuPAD [26]. An implementation of the third order approach in the strongly contracted variant (SC-NEVPT3) has been recently presented [27] and a code with the partially contracted formulation is currently being tested. In the third order calculations carried out thus far [27–30], the third order correction is usually very small in comparison with the second order one. A remarkable exception has been encountered in the study of the Cr_2 potential energy curve [27], where a large third order correction takes place, in some measure upsetting the description obtained at second order and revealing the inadequacy of the zero order description.

The knowledge of the matrix elements of H between the correction functions makes it possible to build a completely variational calculation where the trial wavefunction is expressed as a linear combination in the form

$$\Psi_m^{\text{trial}} = c_0\Psi_m^{(0)} + \sum_{l,k,\mu} c_{l\mu}^{(k)}\Psi_{l,\mu}^{(k)}. \quad (22)$$

In the case of the partially contracted approach such an expansion corresponds to an internally contracted configuration interaction (IC–CI) [31] limited to the single and double contracted excitations of $\Psi_m^{(0)}$. IC–CIs are expected to show the same disadvantages present in the more common single reference SD–CI calculations; in particular they lose the size consistence property enjoyed by the NEVPT approach. An example of IC–CI is provided in Ref. [27], concerning the Cr_2

potential energy curve, where the IC–CI result is shown to parallel the third order description.

6 Implementations of NEVPT

NEVPT has been implemented for the contracted approaches with use of Dyal’s Hamiltonian. SC-NEVPT2 and PC-NEVPT2 have been incorporated in the molecular electronic structure program DALTON [32]. Stand-alone versions of the same codes can be interfaced, besides to DALTON, to the MOLCAS package [33] and this is also the case for the quasidegenerate approach (QD-SCNEVPT2 and QD-PCNEVPT2) and for the third order formulation SC-NEVPT3 (PC-NEVPT3 is being tested at present). All the codes have been parallelized. Furthermore, versions of the programs are available where, in the perturbation expansion, the energy denominators are calculated employing the true Hamiltonian instead of H^D (Epstein–Nesbet denominators): such approach, which is generally lacking in the size consistence property, is occasionally used for comparison purposes. In general a NEVPT2 calculation, no matter whether single state or quasidegenerate, can be done if the corresponding CASSCF is possible. The most important limiting factor in NEVPT2 is given by the size of the active space and by the consequent dimension of the four-particle spinless density matrix. The third order NEVPT can be a rather large calculation, depending on the overall dimension of the orbital basis set, and has been built with a parallelized implementation.

7 An application to the absorption spectrum of free base porphyrin

An important domain of applications of the NEVPT approach is the calculation of the electronically excited states of molecules. Previous studies have concerned the electronic transitions in simple carbonyl compounds [34,35], the Rydberg-valence mixing in the lowest excited states of ethene [21] and formaldehyde [36], the vertical transitions in pyrrole [28], furan [30] and in a model for plastocyanine [37].

In order to show the applicability of the method, we present in this section NEVPT2 calculations for the vertical spectrum of the free base porphyrin molecule.

Due to their central rôle in a great deal of biological phenomena, such as the photosynthesis and the oxygen absorption and transport processes, the photochemical and photophysical properties of the porphyrins have been extensively studied [38–40]. A particular attention has been obviously paid to the experimental and

theoretical investigation of the electronic spectrum of free base porphyrin (FBP), the basic building block of the porphyrins and related systems. Since the FBP has become tractable for correlated theoretical methods, a consistent number of studies has been published, among which we quote the most recent SAC–CI [41–43], STEOM–CC [44,45], MRPT [46,47], MRMP [48] and, finally, TD–DFT [39,49–52] calculations. Certainly, FBP, with its valence π system composed of 24 orbitals and 26 electrons, represents a severe challenge for highly accurate ab initio calculations, at the level, for instance, of coupled cluster or multireference perturbation theory and despite the large number of published studies some spectral assignments are still debated.

The most investigated portion of the absorption spectrum extends from ≈ 2 to ≈ 5.5 – 6.0 eV and is characterized by three principal regions [53–55]. The lowest-energy band (1.98–2.42 eV), the so-called Q band, is composed of two peaks, designated, according to their polarization, as Q_x and Q_y bands. The most intense absorption region, known as Soret Band (or B band) is located in the range between 3.13 and 3.33 eV and a shoulder on its high-energy tail is instead called N band (3.65 eV). Finally, two weak and broad peaks (L and M bands) appear at 4.25 and 5.50 eV.

The traditional interpretation of the first two bands (Q and B) is based on the “four-orbital model” introduced by Gouterman and co-workers [56–58] in the 1960s. According to this model, the low-energy region of the spectrum can be explained in terms of single excitations from the two highest occupied MOs ($5b_{1u}$ and $2a_u$ in the D_{2h} symmetry group) to the two lowest unoccupied MOs ($4b_{2g}$ and $4b_{3g}$) (Fig. 1). So, if the molecule is placed in the xy plane with the x axis passing along the pyrrolic hydrogens, the x and y components of the Q band should be ascribed to the 1^1B_{3u} and 1^1B_{2u} states, respectively; the 2^1B_{3u} and 2^1B_{2u} transitions are instead responsible for the B band. Although Gouterman’s model holds for the interpretation of the Q band, it has proved to fail for the B band, where excitations from the lower b_{1u} orbitals play a non negligible rôle.

The geometry of the ground state of FBP was optimized at B3LYP/6-31G* level, imposing D_{2h} symmetry, which, on the basis of previous theoretical calculations [59,60], was shown to be the most stable one. Following the convention adopted in most previous theoretical works, the molecule has been placed in the xy plane with the two internal hydrogens along the x axis (Fig. 2). All the calculations were carried out with a 6-31G* basis set [61], consisting of 364 basis functions. In the perturbative calculations here reported, the zero order description was attained using two different active

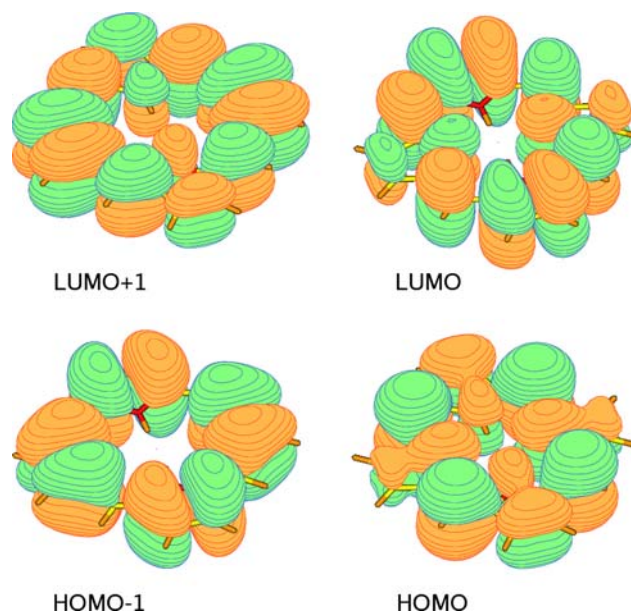


Fig. 1 HOMO ($2a_u$), HOMO-1 ($5b_{1u}$), LUMO ($4b_{3g}$) and LUMO+1 ($4b_{2g}$) MOs of Free Base Porphyrin

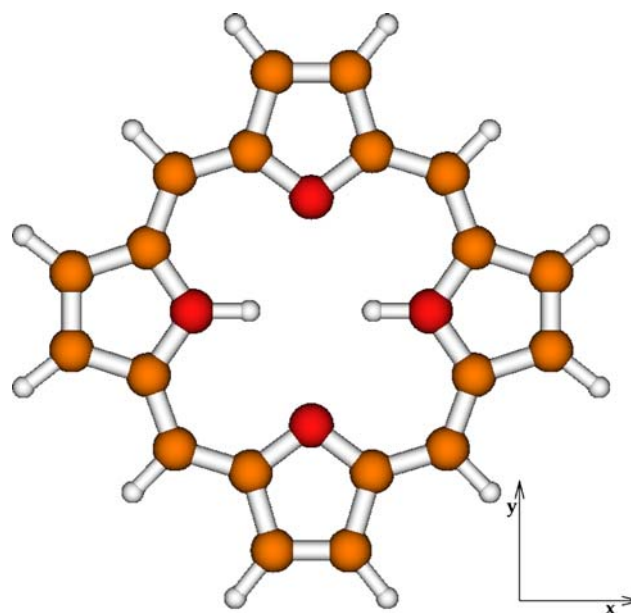


Fig. 2 Molecular structure of Free Base Porphyrin (FBP)

spaces, named CAS(4/4) and CAS(14/13), where the notation (m/n) indicates, as usual, m active electrons and n active orbitals. In all the calculations, the 24 $1s$ orbitals were kept frozen at the CASSCF level. The detailed composition of the two active spaces is given in Table 1, where the number of the computed states is also reported. In the CAS(4/4) calculations the zero order wave function was obtained from single-root CASSCF calculations, whereas with the CAS(14/13) space, state-averaged CASSCF optimizations were performed. The

Table 1 Active spaces, basis set and number of states used in the CASSCF calculations

Basis set	Active space	Composition ^a	Number of states	
			B_{3u}	B_{2u}
6–31G*	CAS(4/4) ^b	$5b_{1u}, 4b_{2g}, 4b_{3g}, 2a_u$	2	2
	CAS(14/13) ^c	$3-5b_{1u}, 3-6b_{2g}, 3-6b_{3g}, 1-2a_u$	4	4

^a At the SCF level the ground state electronic configuration is $20a_g 17b_{3u} 17b_{2u} 14b_{1g} 5b_{1u} 3b_{2g} 3b_{3g} 2a_u$

^b Single-state CASSCF calculations

^c State-averaged CASSCF calculations

excitation energies were obtained with respect to the corresponding ground state 1^1A_{1g} , which was calculated both for the CAS(4/4) and CAS(14/13) spaces.

In Table 2 the CASSCF and NEVPT2 excitation energies are gathered and compared with those computed in the most recent theoretical studies; the experimental data are also reported. Before discussing in detail the interpretation of the spectrum, some general remarks are possible. First of all, contrary to the trend observed in the results of the other ab initio methods [42, 45–47], that, with the exception of the TD–DFT calculations [39, 51], seem to overestimate the correlation energy of the 1^1B_{3u} state with respect to the ground state, the NEVPT2 excitation energies turn out to be slightly higher than the experimental values; a similar behaviour is also noticed for the 1^1B_{2u} state. Also, while a perfect accordance, with differences not exceeding 0.03 eV, can be observed between the SC and PC transition energies in the CAS(4/4) calculation, significant deviations are found using the larger active space. The different behaviour in the second order correction between the two NEVPT variants, can be understood considering the increasing accuracy of the PC approach, involving a much larger number of perturbation functions with respect to the SC case, as the size of the active space increases. Actually, as is apparent, these deviations are more consistent for the higher excited states and the maximum value (0.43 eV) is obtained for the 4^1B_{3u} state. These increasing discrepancies are a clear indicator of the inadequacy of such an active space, including only 13 valence π orbitals (slightly more than half of the complete π valence space), to describe high-energy excited states. Then, it should be considered that the use of molecular orbitals not fully optimized, but obtained from state-averaged calculations, possibly contributes to the defective zero order description.

The most accurate NEVPT results predict the vertical transition to the 1^1B_{3u} and 1^1B_{2u} states at 2.05 and 2.56 eV (CAS(14/13) calculation), in remarkable accordance with the experimental values of 1.98–2.02

(Q_x) and 2.33–2.42 eV (Q_y). Also, we note that, for the Q band, the results obtained from the “four-orbitals” based calculations (CAS(4/4) space) can be regarded as satisfactory. Moreover, the splitting between the 1^1B_{3u} and 1^1B_{2u} states, computed to be 0.47 eV, at the PC level, fully agrees with the observed value of 0.44 eV [55].

If on the one hand the Q band assignment is, altogether, well established, on the other hand the interpretation of the B band is still debated in the literature. In fact, according to Gouterman’s model [56–58] two components, with perpendicular polarizations, should be distinguished: the B_x and B_y bands, arising from the 2^1B_{3u} and 2^1B_{2u} states, respectively. The line splitting between the two components of the B band, measured at low temperature [53], amounts to 0.03 eV. This traditional interpretation, supported by some experimental evidence [54], as well as by the CASPT2 [46, 62], TD–DFT [51] and MRPT [47] calculations, was however questioned by Nakatsuji et al. [41] and Tokita et al. [42], who, on the basis of their SAC–CI calculations, assigned the 2^1B_{3u} state to the B band, but the 2^1B_{2u} state to the N band, appearing as a shoulder to the intense B band. Nevertheless, the SAC–CI oscillator strengths of the two transitions, not matching with the spectrum profile, seem to be a weak point of their conclusions (see Ref. [45]).

The PC-NEVPT2(4/4) results locate the 2^1B_{3u} state at 3.22 eV and the 2^1B_{2u} state at 3.30 eV, predicting a splitting of 0.08 eV, slightly greater than the experimental value of 0.03 eV. A small reduction of this splitting is observed in the CAS(14/13) calculations, where the two states are computed, at the PC level, at 3.30 and 3.35 eV, respectively, in reasonable agreement with experiments (3.13–3.33 eV). While the description of the 2^1B_{2u} state provided by the CAS(4/4) calculations is comparable to that obtained using the larger active space, this is not the case for the 2^1B_{3u} state. Indeed, as shown in Table 3, while, with both active spaces, the reference wavefunction of the 2^1B_{2u} state is dominated by the $5b_{1u} \rightarrow 4b_{3g}$ and $2a_u \rightarrow 4b_{2g}$ configurations, in the larger calculation, the 2^1B_{3u} state is also described by the $4b_{1u} \rightarrow 4b_{3g}$

Table 2 Vertical excitation energies of the first four excited states of B_{3u} and B_{2u} symmetries of free base porphyrin compared with other theoretical results and experimental data

Method	Excited states							
	1^1B_{3u}	1^1B_{2u}	2^1B_{3u}	2^1B_{2u}	3^1B_{3u}	3^1B_{2u}	4^1B_{3u}	4^1B_{2u}
CAS(4/4)								
CASSCF	3.48	3.71	5.08	5.12				
SC-NEVPT2	2.05	2.53	3.25	3.33				
PC-NEVPT2	2.04	2.51	3.22	3.30				
CAS(14/13)								
CASSCF	3.12	3.80	4.72	5.22	5.74	6.15	7.52	6.27
SC-NEVPT2	2.21	2.76	3.49	3.62	4.10	4.40	4.93	4.47
PC-NEVPT2	2.05	2.56	3.30	3.35	3.84	4.13	4.50	4.10
Previous works								
CASPT2 [46]	1.63	2.11	3.12	3.08	3.53	3.42	4.04	3.96
MRPT2 [47]	1.73	2.25	2.96	3.02				
SAC-CI [42]	1.75	2.23	3.56	3.75	4.24	4.52	5.45	5.31
STEOM-CC [45]	1.72	2.61	3.66	3.77	4.28	4.67	5.38	5.26
TD-DFT [51]	2.16	2.29	2.98	3.01	3.47	3.41	3.76	3.77
TD-DFT [39]	2.27	2.44	3.33	3.41	3.61	3.56	3.89	3.89
Expt. values								
Assignment	1.98–2.02 ^a Q _x	2.33–2.42 ^a Q _y	3.13–3.33 ^b B _x	3.13–3.33 ^b B _y	3.65 ^c N		4.25 ^c L	

^a Refs. [55,63,64]^b Refs. [53,55,64]^c Ref. [55]

excitation (22%), not considered in Gouterman's four-orbital model.

The interpretation of the two higher-energy bands is certainly more complex and also the experimental evidence is less clear. Moreover, as shown by Gwaltney and Bartlett [45], in this region of the spectrum (4.5–5 eV) the Rydberg transitions are expected to start. By now, the firmest assignment, suggested by Serrano-Andrés et al. [46], is that the N band has to be ascribed to the pair of states 3^1B_{3u} – 3^1B_{2u} and, analogously, the so-called L band is assigned to the 4^1B_{3u} – 4^1B_{2u} states. However, as apparent in Table 2, quite a conflicting picture emerges from the results of the various theoretical methods, with differences in the computed excitation energies greater than 1 eV. At the partially contracted level, the 3^1B_{3u} – 3^1B_{2u} states are computed at 3.84–4.13 eV, whereas the other pair of states 4^1B_{3u} – 4^1B_{2u} is located at 4.50–4.10 eV. Our results, over all, are consistent with the CASPT2 interpretation, since the largest deviation between the PC-NEVPT2 and CASPT2 amounts roughly to 0.7 eV (3^1B_{2u} state). Nevertheless, a too sizable splitting, with respect to that computed by Serrano-Andrés et al. [46], is found between the components of each pair of states. However, at the present stage

of calculation, since the ground state geometry, basis set and, above all, the active space used for this study are not the same as in Ref. [46], and hence also the nature of the excited states computed is not exactly the same, the direct comparison with the CASPT2 results should be regarded with care.

8 Conclusions

This article has been concerned with an analysis of the main features and developments of the NEVPT approach. The various possibilities which arise from the utilization of correction functions with different degree of contraction and from the use of either the true or a model Hamiltonian, have been considered. While the totally uncontracted approaches, even with the simplification afforded by the use of Dyal's model Hamiltonian, appear as computationally too expensive, the adoption of contracted perturbations has led to a viable and efficient MRPT. The partially contracted and the strongly contracted formulations of NEVPT with the use of Dyal's Hamiltonian, have been shown to be endowed with the two remarkable properties of size consistence

Table 3 Analysis of the CASSCF wave function composition

State	CAS(4/4)		CAS(14/13)		State	CAS(4/4)		CAS(14/13)	
	Config.	Weight (%)	Config.	Weight (%)		Config.	Weight (%)	Config.	Weight (%)
1^1B_{3u}	$5b_{1u} \rightarrow 4b_{2g}$	43	$5b_{1u} \rightarrow 4b_{2g}$	46	1^1B_{2u}	$5b_{1u} \rightarrow 4b_{3g}$	40	$5b_{1u} \rightarrow 4b_{3g}$	41
	$2a_u \rightarrow 4b_{3g}$	55	$2a_u \rightarrow 4b_{3g}$	42		$2a_u \rightarrow 4b_{2g}$	58	$2a_u \rightarrow 4b_{2g}$	51
2^1B_{3u}	$5b_{1u} \rightarrow 4b_{2g}$	52	$5b_{1u} \rightarrow 4b_{2g}$	25	2^1B_{2u}	$5b_{1u} \rightarrow 4b_{3g}$	55	$5b_{1u} \rightarrow 4b_{3g}$	43
	$2a_u \rightarrow 4b_{3g}$	39	$4b_{1u} \rightarrow 4b_{2g}$	22		$2a_u \rightarrow 4b_{2g}$	36	$2a_u \rightarrow 4b_{2g}$	37
			$2a_u \rightarrow 4b_{3g}$	35					
3^1B_{3u}			$5b_{1u} \rightarrow 4b_{2g}$	37	3^1B_{2u}			$4b_{1u} \rightarrow 4b_{3g}$	56
			$4b_{1u} \rightarrow 4b_{2g}$	34				$3b_{1u} \rightarrow 4b_{3g}$	20
			$2a_u \rightarrow 4b_{3g}$	9					
4^1B_{2u}			$3b_{1u} \rightarrow 4b_{2g}$	87	4^1B_{2u}			$4b_{1u} \rightarrow 4b_{3g}$	66
								$5b_{1u} \rightarrow 4b_{3g}$	14

Only the configurations with weight greater than 5% are considered

and absence of intruder states. The relatively low number of correction functions and the possibility of a practical and efficient evaluation of the matrix elements of the Hamiltonian between internally contracted functions, has made it possible to open the way to the third order NEVPT formulation and to a form of internally contracted configuration interaction. In order to show the applicability of the NEVPT approach to a non trivial case, the calculation of the vertical excitation spectrum of the biologically important free base porphyrin molecule has been presented, showing good accordance with previous theoretical evaluations and with experiment.

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