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REGULAR ARTICLE

**Celestino Angeli · Renzo Cimiraglia**
**Jean-Paul Malrieu**

# A simple approximate perturbation approach to quasi-degenerate systems

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**Abstract** In this paper a simple approximate approach for the study of quasi-degenerate systems is presented in the frame of multireference perturbation theory. The formulation can be considered as an approximation of the quasi-degenerate perturbation theory (QDPT) with the simplification that only the state specific (diagonal) perturbation corrections to the energy have to be computed. The new approach is discussed and compared with previous QDPT formulations using the weakly avoided crossing model (for which new properties are here presented) and applied to the case of the neutral/ionic energy crossing in the LiF molecule.

**Keywords** Quasi-degenerate Perturbation theory · Multireference CI · Perturbation CI · NEVPT

## 1 Introduction

In many chemically important circumstances one has to face the problem of the description of a certain number of quasi-degenerate electronic states. Strictly avoided crossings of electronic states, conical intersections, valence/Rydberg mixing in $\pi \rightarrow \pi^*$ excited states of many organic compounds, are common examples of quasi-degenerate systems of great importance in Chemistry.

We shall suppose that $n$ electronic states of a system are quasi-degenerate and that the zero-order description is obtained by the diagonalization of the Hamiltonian in a given subspace, $S$, of the full-CI space (FCI)

$$P_S \hat{\mathcal{H}} P_S \Psi_m^{(0)} = E_m^{(0)} \Psi_m^{(0)}, \tag{1}$$

where $P_S$ is the projector onto the $S$ space and $\Psi_m^{(0)}$, $E_m^{(0)}$ are the zero-order wavefunctions and energies. The $S$ space can be defined on the basis of a predefined excitation level, such as single and double CI (SDCI) [1], or of the choice of a FCI space in a restricted orbital set (complete active space, CAS) [2,3] or of a selection procedure to build up the determinant space [4].

The $\Psi_m^{(0)}$ wavefunctions are linear combinations of configuration state functions, CSF, or determinants ($\phi_k$, $1 \leq k \leq N$, with $N$ the dimension of the $S$ space)

$$\Psi_m^{(0)} = \sum_{k=1}^{N} c_k^m \phi_k. \tag{2}$$

In a state-specific perturbation approach, the energy is corrected to the second-order

$$E_m^{(2)} = \sum_i \frac{\left|\left\langle \Psi_m^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_i^{(0)} \right\rangle\right|^2}{E_m^{(0)} - E_i^{(0)}}, \tag{3}$$

where the index $i$ runs over the zero-order wavefunctions outside the $S$ space which interact with $\Psi_m^{(0)}$. It is well known that this approach fails in the case of quasi-degenerate states. In diatomic molecules, for instance, in the case of states showing a weakly avoided crossing, a double-crossing can be found at the perturbation level [5,6]. Other examples of quasi-degeneracy are the valence/Rydberg excited states in spectroscopy and the conical intersections in photochemistry. In such cases the quasi-degenerate perturbation theory (QDPT) must be applied. Here, for the reader's convenience, only a sketch of the QDPT approach will be given. In the QDPT scheme, an effective Hamiltonian, $\hat{\mathcal{H}}_{\text{eff}}$, is built on a model space which is chosen so that it contains the main part of the relevant quasi-degenerate states. $\hat{\mathcal{H}}_{\text{eff}}$ is expanded in a perturbation series: the sum of the zero- and first-order terms coincide with the projection of the Hamiltonian in the model

C. Angeli (✉) · R. Cimiraglia
Dipartimento di Chimica, Università di Ferrara,
Via Borsari 46, I-44100 Ferrara, Italy
E-mail: anc@unife.it

J-P. Malrieu
IRSAMC, Laboratoire de Physique Quantique,
Université Paul Sabatier,
118 route de Narbonne, 31062 Toulouse Cedex, France

space, while the second-order matrix elements are:

$$\left\langle \Psi_n^{(0)} \left| \hat{\mathcal{H}}_{\text{eff}}^{(2)} \right| \Psi_m^{(0)} \right\rangle = \sum_i \frac{\left\langle \Psi_n^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_i^{(0)} \right\rangle \left\langle \Psi_i^{(0)} \left| \hat{\mathcal{H}} \right| \Psi_m^{(0)} \right\rangle}{E_m^{(0)} - E_i^{(0)}}. \tag{4}$$

The off-diagonal coupling terms of $\hat{\mathcal{H}}_{\text{eff}}^{(2)}$ allow the model wavefunctions to mix with different ratios and therefore to revise the zero-order description of the relevant states taking into account the perturbation effects. This is particularly important when mixing of configurations with different electronic nature (such as for instance Rydberg, valence, ionic, neutral states) is expected in the system under study. In this case the mixing ratio found at the zero-order level (e.g., CAS-CI) could be strongly defective, due to the lack of the dynamic correlation. Indeed the dynamic correlation energy, being normally different for electronic distributions of a different nature, can change the mixing ratio considerably.

The computational implementation of the QDPT approach is not always straightforward, as happens for instance in the case of perturbation theories with state-specific partitions of the Hamiltonian where the multipartitioning technique of Zaitsevskii and Malrieu [7] must be adopted (two examples are the QD *n*-electron valence state perturbation theory, QD-NEVPT2 [8], and the multi-state complete active space perturbation theory, MS-CASPT2 [9]). For these reasons an approach able to treat quasi-degenerate states and based only on the knowledge of the second order diagonal correction to the energy [Eq. (3)] can be of interest even if approximate. Such an approach is presented in the successive sections under the name of n-QDPT (n standing for naïve).

The rest of this paper is organized as follows: in the successive section the mathematical formulation of the n-QDPT scheme is presented, in Sect. 3 it is used to study the weakly avoided crossing model (WACM) [10] and in Sect. 4 its application to the neutral/ionic crossing in LiF is discussed.

## 2 Mathematical formulation

Let us consider a subspace of $S$ spanned by a set of $M$ linearly independent functions hereafter indicated collectively with $\Phi$. The functions $\Phi_k$ could be CSFs (determinants) or in general liner combinations of CSFs (as, e.g., diabatic states). They are supposed to give a good, at least qualitatively, description of the $m$ quasi-degenerate states of interest and to be orthonormal. Another requirement for this $\Phi$ will be formalized in the following. Consider the projection of $\Psi_m^{(0)}$ onto the space spanned by $\Phi$

$$\Psi_m^{(0)\prime} = P_\Phi \Psi_m^{(0)} = \sum_{k=1}^{M} C_k^m \Phi_k, \tag{5}$$

($P_\Phi$ is the projector onto $\Phi$). The coefficients $C_k^m$ are possibly renormalized so that

$$\left\langle \Psi_m^{(0)\prime} \mid \Psi_m^{(0)\prime} \right\rangle = 1. \tag{6}$$

We now define a (non-hermitian) $\hat{\mathcal{H}}_{\text{eff}}$ such that its zero-order part, $\hat{\mathcal{H}}_{\text{eff}}^{(0)}$, is

$$\hat{\mathcal{H}}_{\text{eff}}^{(0)} \Psi_m^{(0)\prime} = E_m^{(0)} \Psi_m^{(0)\prime}. \tag{7}$$

In the $\Psi'$ set the matrix elements of $\hat{\mathcal{H}}_{\text{eff}}^{(0)}$ are

$$\left\langle \Psi_n^{(0)\prime} \left| \hat{\mathcal{H}}_{\text{eff}}^{(0)} \right| \Psi_m^{(0)\prime} \right\rangle = S_{nm} E_m^{(0)}, \tag{8}$$

with

$$S_{nm} = \sum_{K=1}^{M} C_k^m C_k^n. \tag{9}$$

In the $\Phi$ set we have

$$\left\langle \Phi \left| \hat{\mathcal{H}}_{\text{eff}}^{(0)} \right| \Phi \right\rangle = \mathbf{C}^{-1\dagger} \left\langle \Psi' \left| \hat{\mathcal{H}}_{\text{eff}}^{(0)} \right| \Psi' \right\rangle \mathbf{C}^{-1}, \tag{10}$$

with $\Psi' = \Phi\mathbf{C}$. The zero-order description of $\hat{\mathcal{H}}_{\text{eff}}$ is then corrected by adding a second-order contribution, $\hat{\mathcal{H}}_{\text{eff}}^{(2)}$, which is supposed to be diagonal in the $\Phi$ basis. This hypothesis is not true in general and therefore it can be a drastic approximation. As said before, the CAS-CI wavefunctions for instance could not satisfy this request in the case of quasi-degenerate states. An empirical criterion to be followed for the $\Phi_k$s in order to render this approximation less drastic is that they should have a clear physical nature. In this case one can suppose that the off diagonal elements of $\hat{\mathcal{H}}_{\text{eff}}$ are not strongly affected by the electronic correlation and thus are correctly described at the zero-order level. The diagonal elements of $\hat{\mathcal{H}}_{\text{eff}}^{(2)}$ are obtained by solving the set of linear equations

$$E_m^{(2)} = \sum_{k=1}^{M} \left(C_k^m\right)^2 \left(\hat{\mathcal{H}}_{\text{eff}}^{(2)}\right)_{kk}, \tag{11}$$

where $E_m^{(2)}$ is the second-order correction to the energy for the $m$-th state, obtained in a state-specific multireference perturbation theory approach, such as for instance NEVPT2 [11–13], CASPT2 [14,15], CIPSI [4,16–18], etc. Note that Eq. (11) can be solved if the matrix collecting the elements $\left(C_k^m\right)^2$ is not singular: in the case of a two-state problem, if $\Phi_1$ and $\Phi_2$ have equal weight in the two zero-order wavefunctions $\Psi_1^{(0)}$ and $\Psi_2^{(0)}$, Eq. (11) does not have a solution. This problem should be met in principle on a restricted set of nuclear geometries, which must therefore be discarded in actual calculations.

After such corrections are computed, the matrix $\left\langle \Phi \left| \hat{\mathcal{H}}_{\text{eff}}^{(0)} + \hat{\mathcal{H}}_{\text{eff}}^{(2)} \right| \Phi \right\rangle$ is diagonalized

$$\left\langle \Phi \left| \hat{\mathcal{H}}_{\text{eff}}^{(0)} + \hat{\mathcal{H}}_{\text{eff}}^{(2)} \right| \Phi \right\rangle \tilde{\mathbf{C}}_m = \tilde{E}_m \tilde{\mathbf{C}}_m. \tag{12}$$

The energies $\tilde{E}_m$ and the wavefunctions

$$\tilde{\Psi}_m = \sum_{k=1}^{M} \tilde{C}_k^m \Phi_k, \tag{13}$$

are approximations of those obtained in the usual QDPT formalisms.

## 3 The weakly avoided crossing model

In this section we use the WACM proposed by Malrieu *et al.* [10] to comment on the approximate n-QDPT approach presented in the previous section. Briefly, in the WACM the FCI space is spanned by three functions $\phi_1$, $\phi_2$ and $\phi_3$ describing a one-dimensional system (with the variable $r$) and the Hamiltonian matrix in this basis has the form

$$\mathbf{H} = \begin{bmatrix} 0 & h & K \\ h & ar & 0 \\ K & 0 & \Delta \mathrm{E} \end{bmatrix}, \tag{14}$$

with the hypothesis that $\Delta E > ar$ and $0 < K \ll \Delta E$. In this model the energies associated with $\phi_1$ and $\phi_2$ cross at $r = 0$: the coupling $h$ between them makes this an avoided crossing. The third state, $\phi_3$, much higher in energy, interacts only with $\phi_1$. In a perturbative scheme, where the effect of $\phi_3$ is considered as a small perturbation, the energy of the first state is lowered by $\simeq -K^2/\Delta E$ while for the second state the energy does not change. The crossing is therefore expected at $r \simeq -K^2/a\Delta E$. Defining the crossing point as the distance $r_c$ where the coefficients of $\phi_1$ and $\phi_2$ are equal, one gets

$$ar_c = \frac{\Delta E - h}{2}\left(1 - \sqrt{1 + \frac{4K^2}{(\Delta E - h)^2}}\right), \tag{15}$$

or expanding in power of $(\Delta E - h)^{-1}$,

$$ar_c = -\frac{K^2}{\Delta E - h} + \frac{K^4}{(\Delta E - h)^3} - \frac{2K^6}{(\Delta E - h)^5} + \cdots . \tag{16}$$

Let us note that the expansion published in Ref. [10] is slightly different, being in power of $\Delta E^{-1}$ but the present one results in a more compact form. The energy of the two lowest states at the crossing point is

$$E_1 = ar_c - h \quad \text{and} \quad E_2 = ar_c + h \tag{17}$$

In Ref. [10], the WACM has been used to discuss various versions of the perturbation theory: QDPT in the basis of determinants, prediagonalization of the 2 × 2 model space followed by non-degenerate perturbation treatment, QDPT in the basis of the eigenfunctions of $\hat{\mathcal{H}}$ in the 2 × 2 model space and the use of intermediate effective Hamiltonians [19].

In order to apply the n-QDPT approach, let us first simplify the formulation of the problem, by scaling the matrix elements of $\hat{\mathcal{H}}$ by $h^{-1}$, so that

$$\mathbf{H} = \begin{bmatrix} 0 & 1 & k \\ 1 & x & 0 \\ k & 0 & e \end{bmatrix} \quad \text{with} \quad \begin{array}{l} k = K/h \\ x = ar/h \\ e = \Delta E/h \end{array} . \tag{18}$$

The $S$ space is spanned by $\phi_1$ and $\phi_2$, and so the two zero-order energies and wavefunctions are

$$\begin{aligned} E_1^{(0)} &= \frac{x - \sqrt{4 + x^2}}{2}, \\ E_2^{(0)} &= \frac{x + \sqrt{4 + x^2}}{2}, \\ \Psi_1^{(0)} &= c_1^1\, \phi_1 + c_2^1\, \phi_2, \\ \Psi_2^{(0)} &= c_1^2\, \phi_1 + c_2^2\, \phi_2, \end{aligned} \tag{19}$$

with

$$\begin{aligned} c_1^1 &= -\sqrt{\frac{4 + x^2 + x\sqrt{4 + x^2}}{2\left(4 + x^2\right)}}, \\ c_2^1 &= \sqrt{\frac{2}{4 + x^2 + x\sqrt{4 + x^2}}}, \\ c_1^2 &= \sqrt{\frac{4 + x^2 - x\sqrt{4 + x^2}}{2\left(4 + x^2\right)}}, \\ c_2^2 &= \sqrt{\frac{2}{4 + x^2 - x\sqrt{4 + x^2}}}. \end{aligned} \tag{20}$$

In this case the wavefunctions $\phi_1$ and $\phi_2$ define also the set $\Phi$: therefore the zero-order effective Hamiltonian in the $\Phi$ basis is simply

$$\mathbf{H}_{\mathrm{heff}}^{(0)} = \begin{bmatrix} 0 & 1 \\ 1 & x \end{bmatrix}. \tag{21}$$

The second-order corrections to the energy for the two states are

$$\begin{aligned} E_1^{(2)} &= \frac{\left(c_1^1\right)^2 k^2}{\frac{x - \sqrt{4 + x^2}}{2} - e} \\ &= \frac{k^2}{4 + x^2}\,\frac{4 + x^2 + \sqrt{4 + x^2}}{x - 2e - \sqrt{4 + x^2}}, \end{aligned} \tag{22}$$

$$\begin{aligned} E_2^{(2)} &= \frac{\left(c_1^2\right)^2 k^2}{\frac{x + \sqrt{4 + x^2}}{2} - e} \\ &= \frac{k^2}{4 + x^2}\,\frac{4 + x^2 - \sqrt{4 + x^2}}{x - 2e + \sqrt{4 + x^2}}. \end{aligned} \tag{23}$$

The solution of the system of linear equations (11), gives the diagonal terms of the second-order correction to $\hat{\mathcal{H}}_{\mathrm{eff}}$

$$\left(\hat{\mathcal{H}}_{\mathrm{eff}}^{(2)}\right)_{11} = \frac{k^2\left(1 - ex + x^2\right)}{e^2x - x - ex^2}, \tag{24}$$

$$\left(\hat{\mathcal{H}}_{\mathrm{eff}}^{(2)}\right)_{22} = -\frac{k^2}{x\left(e^2x - x - ex^2\right)}, \tag{25}$$

and the expression of $\hat{\mathcal{H}}_{\mathrm{eff}}$ to the second order is

$$\mathbf{H}_{\mathrm{heff}}^{(0+2)} = \begin{bmatrix} \frac{k^2\left(1 - ex + x^2\right)}{\left(e^2x - x - ex^2\right)} & 1 \\ 1 & x - \frac{k^2}{\left(e^2x - x - ex^2\right)} \end{bmatrix}.$$

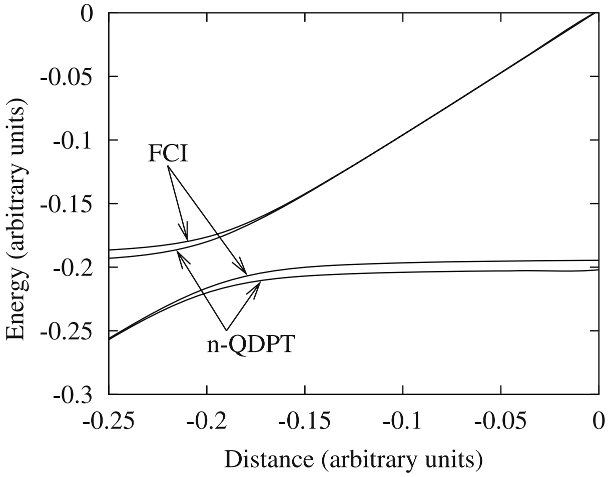

**Fig. 1** Comparison of the first two potential energy curves of the WACM obtained at the FCI and n-QDPT level

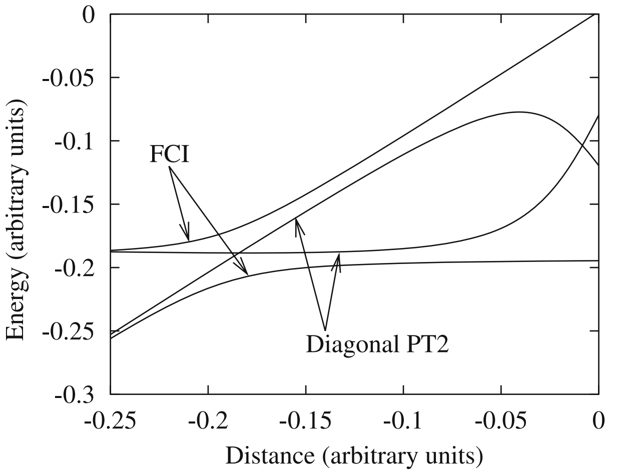

**Fig. 2** Comparison of the first two potential energy curves of the WACM obtained at the FCI and diagonal PT2 level

The crossing point, $x_c$, is obtained by solving

$$k^2\left(1-ex_c+x_c^2\right)=x_c\left(e^2x_c-x_c-ex_c^2\right)-k^2 \qquad (26)$$

but the analytical expression of $x_c$ is not trivial. One can however, as in the FCI case, suppose that $x_c$ is expanded in powers of $e^{-1}$ and considering only the terms proportional to $e^0$ in Eq. (26), one gets

$$k^2(1-ex)=e^2x^2-k^2 \qquad (27)$$

which is solved for $x_c = -k^2/e$ in agreement with the FCI result.

In order to compare the n-QDPT results with the FCI ones, they are reported in Fig. 1 for a case with $h = 0.02$, $K = 1$, $\Delta E = 5$ and $a = 1$ in a region around the crossing point. With these parameters the FCI crossing occurs for $r = -0.1933$ where the FCI energies are $E_1 = -0.2133$ and $E_2 = -0.1733$. The diagonal second-order correction ($E_1^{(2)}$ and $E_2^{(2)}$) are reported in Fig. 2.

It can be noted that the non-degenerate second-order corrections (Fig. 2) show a wrong behavior, with two actual crossings, one occurring close to zero (the avoided crossing at the zero order is at $r = 0$) and the other close to the FCI avoided crossing. This anomaly is effectively corrected by the n-QDPT approach as shown in Fig. 1. As noted in Sect. 2, the system of linear equations cannot be solved if the matrix collecting the squared coefficients is singular. In the present case this happens for $r = 0$ where all the elements of such matrix are equal to 0.5. However, in the example presented here the results are numerically stable for values of $r$ very close to 0 ($|r| \geq 0.01$) thus allowing the construction of the full potential energy curves.

For the sake of clarity, the first two curves obtained with the QDPT on the basis of the $\phi_1$, $\phi_2$ and $\phi_3$ functions [QDPT(det)] and on the basis of the eigenfunctions of $\hat{\mathcal{H}}$ [QDPT(diag)] are reported in Fig. 3. From the comparison with Fig. 1 one notes that the n-QDPT is a good approximation to the standard QDPT.

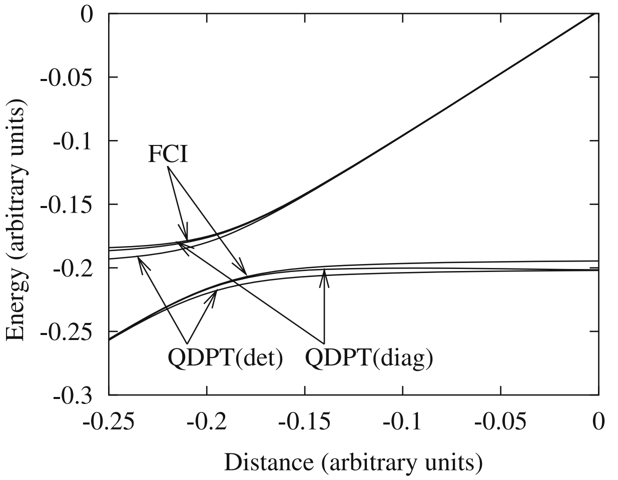

**Fig. 3** Comparison of the first two potential energy curves of the WACM obtained at the FCI and QDPT on the basis of the $\phi_1$, $\phi_2$ and $\phi_3$ functions [QDPT(det)] and on the basis of the eigenfunctions of $\hat{\mathcal{H}}$ [QDPT(diag)]

## 4 The neutral/ionic crossing in LiF

The n-QDPT approach has been applied also on a real system. The neutral/ionic crossing in the LiF has been often chosen as a test problem [8,10,20–24] for new methods designed to treat quasi-degenerate states, given that it has a relatively modest size, that an FCI study has been published [20] and that there is a clear physical description of the curves showing the crossing. Indeed, as in other alkali halides [25], the neutral Li· + ·F and the ionic $\mathrm{Li}^+$ + :$\mathrm{F}^-$ diabatic curves cross at a distance which is a function of the ionization potential of the alkali atom, of the electron affinity of the halogen and of the polarizability of both atoms [26,27].

The basis set Li($9s5p$)/[$4s2p$] F($9s6p1d$)/[$4s3p1d$], employed by Bauschlicher and Langhoff [20] for an FCI study, is used in the present calculations. The zero-order wavefunctions have been obtained by a state-averaged CASSCF

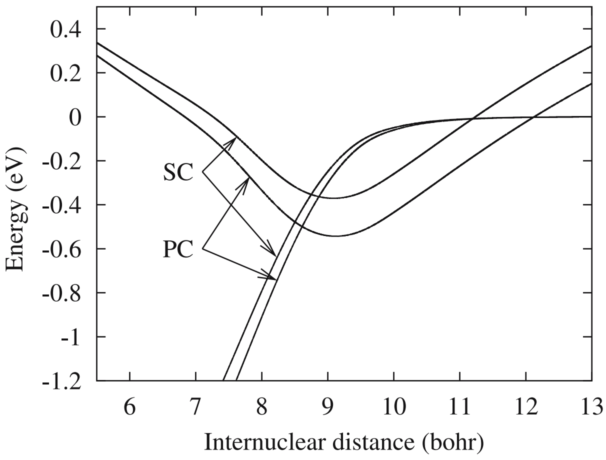

**Fig. 4** Comparison of the first two potential energy curves of LiF obtained with the state-specific SC and PC variants of NEVPT2

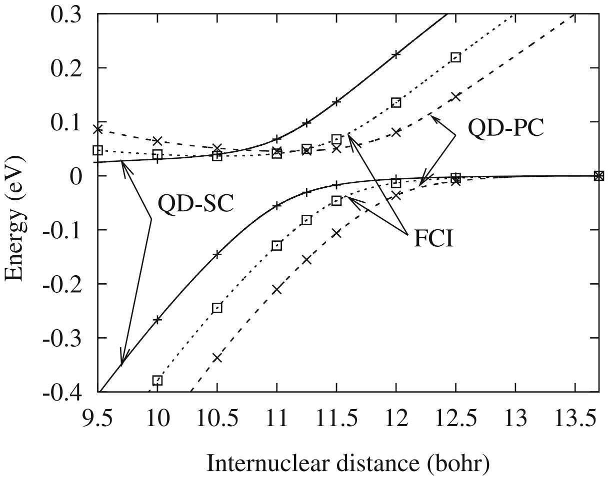

**Fig. 5** Comparison of the first two potential energy curves of LiF obtained with the QDPT formulation of of NEVPT2

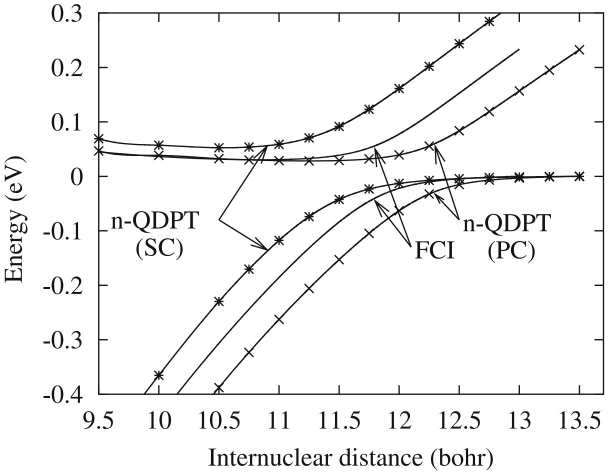

**Fig. 6** Comparison of the first two potential energy curves of LiF obtained with the n-QDPT approach applied to the SC and PC variants of NEVPT2

procedure, involving the ground and the first $^1\Sigma^+$ excited states, using the Molcas package [28]. The active space contains the Li $2s$ and F $2p_z$, $2p_x$ and $2p_y$ valence orbitals, plus two correlating $2p'_x$ and $2p'_y$ virtual orbitals (CASSCF 6/6). The $1\sigma$, $2\sigma$ and $3\sigma$ orbitals are kept frozen, in the CASSCF procedure, at the CASSCF 2/2 (Li $2s$ and F $2p_z$) level in order to allow the comparison with the FCI results.

At the CASSCF level the avoided crossing takes place at an internuclear distance which turns out to be too short because of the lack of dynamic correlation energy that is more pronounced for the ionic form with respect to the neutral one [8].

The state-specific strongly contracted (SC) and partially contracted (PC) variants of NEVPT2 [11–13] have been used to correct the zero-order energies, keeping the $1\sigma$, $2\sigma$ and $3\sigma$ frozen in the correlation treatment. The SC and PC NEVPT2 energies are reported in Fig. 4. As expected [8,10,21], the curves show a double-crossing instead of an avoided crossing, which, at the FCI level, is located around 12 bohr.

In order to solve this problem, our group has recently applied the quasi-degenerate version of NEVPT2 (QD-NEVPT2) to this system [8], obtaining a satisfactory agreement with the FCI results (see Fig. 5).

The purpose here is to verify if the approximate n-QDPT approach is able to extract from the two second-order corrections to the energy the main physical effects and thus to recover the correct behavior. To this aim, the correct identification of the model functions ($\Phi_1$ and $\Phi_2$ in the present case) is crucial. In the case of LiF the natural choice is to use the closed shell ionic determinant and the singlet combination of the two open-shell neutral determinants. Let us note that in order to ensure the identification of the relevant determinants, care must be taken to avoid that the molecular orbitals, on which the determinants are built, strongly change in nature along the internuclear coordinate.

The n-QDPT approach described in Sect. 2 has been applied to LiF, using the CASSCF, SC and PC NEVPT2 energies and the coefficients of the model determinants in the two CASSCF wavefunctions as input data. The results are reported in Fig. 6, from which one notes that the n-QDPT energies behave correctly, showing an avoided crossing in a region where the FCI crossing is observed. In this case the matrix collecting the squared coefficients has fortuitously never been found to be singular (there exists at least one internuclear geometry where this happens). The n-QDPT curves show the main characteristics of the QD-NEVPT2 ones [8], reported in Fig. 5.

## 5 Conclusion

This work has presented an approximate approach, n-QDPT, to study systems with quasi-degenerate levels. The application of n-QDPT to two test problems indicates that this approach, its simplicity and approximation notwithstanding, is endowed with a strong physical content, being able to extract from the misbehaving diagonal corrections to the energy a correct effective Hamiltonian. Due to the very simple formulation, the n-QDPT results can be obtained in various manners (through computer algebra systems such as, e.g, Mupad [29], Mathematica [30], and Maple [31]) using only few output data of a perturbation calculation. In this way it is possible to avoid the heavy computational implementation, usually required for a quasi-degenerate approach to PT. It is worth remarking that n-QDPT can be applied to the results of any perturbation theory. For these reasons, n-QDPT could represent a reliable alternative when a quasi-degenerate version of a PT is not available.

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