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Propagator matrices as matrices of power's series. II. It's relationship with HF's stability problem and alternative solutions

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Abstract

Some non-singlet quasi-instabilities (QIs) cases that arise in the calculation of NMR-*J* parameters are analyzed within response theory. The relationship between 'very close to zero' eigenvalues of the principal propagator and the rate of convergency for specific coupling pathways is shown by a power series implemented to calculate the principal propagator matrix. A natural criterion for the analysis of the stability problem emerges from that series. This is more general and accurate compared with previous proposals. Its relationship with π-type molecular orbitals is given. We present an alternative scheme to minimize the effects of non-singlet QIs in such a way that the NMR-*J* parameters become close to the best theoretical calculations for H_2CX ($X = CH_2$, NH and O).

Keywords: Quasi-instability; Propagator matrix; Random phase level of approach; NMR-J parameter

1. Introduction

The theoretical study of the NMR-*J* spectroscopic parameter in compounds which are of interest for organic and inorganic chemistry is many times plagued with problems of instabilities or quasi-instabilities (QI) when the calculations are done at the random phase level of approach (RPA). If the molecular system has a π-electronic framework, it is very likely that it will produce at least QI problems when calculations of *J* are done at that level [1,2]. There are also some other model compounds for which *J* calculations cannot be done at RPA level even when they are saturated [3]. Previous works have shown that there are two general strategies to overcome this problem: (i) by using post-RPA schemes or (ii) applying a more crude approach. This is equivalent to say that one should go in opposite directions including more or less electron correlation in the calculations. The first case is applied mainly on ab initio methods and for that reason the size of model compounds to which it could be worked on is reduced to small molecules. The second alternative is used with semiempirical methods but its results are in that case much less accurate. Then it should be convenient to explore a different strategy to overcome or minimize QI problems.

It is important to point out that semiempirical schemes are designed in such a way that they use some empirical parameters to fit theoretical results

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with experiments. This means that electron correlation is included in a suitable, though unsystematic, way. This explain why semiempirical calculations of NMR-J parameters fit at least in a qualitative (some time semiquantitative) way with experimental results.

In a previous paper [4] called Part I throughout we presented a new methodology to calculate the NMR-J parameter within response theory. It was shown that at RPA level of approach each matrix element of the principal propagator matrix can be expressed as a power series and have a different rate of convergency. It depends on the molecular system being analyzed and strongly on the molecular orbitals (MOs) (two occupied and two vacants) involved in that particular matrix element. They can be localized resembling chemical functions like bonding, anti-bonding and lone pairs.

The linear response calculations of nuclear magnetic coupling constant at RPA level is equivalent to the finite perturbation theory (FPT) [5], and the self-consistent perturbation theory (SCPT) [6,7]. In both cases, a QI problem manifest itself as a very low rate of convergence in the iterative procedure [8]. In the case of the principal propagator matrix built up from series each matrix element is written as a power series with a proper rate of convergence. It means that there should be an intrinsic relationship of these three schemes. The last one gives a deeper insight in order to analyze in more detail the effects of QI on calculations of electron spin-dependent molecular properties.

The main goal of this paper which is intended to tackle non-singlet QIs, will focus on: (i) the specific excitation of MOs involved, (ii) the most adequate parameters that can be chosen in order to determine 'when' a calculation will be plagued with QI problems before of doing it and (iii) whether there are more efficient and cheaper alternatives to minimize QI problems. Applying the scheme mentioned above, we are able to identify which is (are) the specific matrix element(s) which produce large disturbs in the inversion process of the principal propagator matrix when QI problems are present. We found an alternative procedure to minimize QIs getting reliable results for couplings which do not depend much on the electronic framework which produce that QIs. It is based on avoiding one of the integrals $(aj|bi)$ or $(ab|ji)$ in the problematic matrix element, say $\{NE^{-1}\}_{ia,jb}$ (Section 2). We apply this proposal on three unsaturated molecular models with extreme non-singlet QIs, and on a saturated molecule with moderate QI. Studying $H_2C{=}X$ molecular models we show that we can obtain results that are close to the best theoretical results calculated with ab initio methods. In this manner our scheme can be applied with confidence in larger molecular systems.

Previous works gave either the difference HOMO–LUMO or the smallest eigenvalue of the principal propagator matrix as the criteria to evaluate 'when' a calculation could be affected by QI problems [9]. Another aim of this paper is to show that there is another criterion which answers more accurately that query.

In Section 2 we give an outline of the theory necessary for understanding QI problems and J calculations using polarization propagator matrix elements as a series. Results are given in Section 3 where we analyze ratios of convergence and propose a small and specific modification to minimize QI. Concluding remarks are given in Section 4.

2. Theory

The problem of the stability condition of the restricted Hartree–Fock (RHF) electronic ground state of a molecular system is closely related to RPA [3]. The RHF ground state is not the most general independent particle ground state owing to the restrictions imposed on it, e.g. to be real and singlet state. The condition that must be satisfied to ensure that the energy remains a minimum when any of these restrictions is relaxed is that the matrices $({}^m\mathbf{A} \pm {}^m\mathbf{B})$ must be positive definite [3].

Non-singlet (or triplet) 'instabilities' correspond to the case in which a triplet state has a lower energy than the RHF ground state. In this case, at least one eigenvalue of the triplet propagator $({}^3\mathbf{A} - {}^3\mathbf{B})$ matrix is negative, and it is said that the whole system is non-singlet unstable. In this case it is not possible to calculate Fermi contact (FC) and spin dipolar (SD) contributions to the coupling constant J. This is one of the more frequent problems that affect the indirect nuclear spin coupling constant calculations.

When all eigenvalues of the $({}^3\mathbf{A} - {}^3\mathbf{B})$ matrix are positive, but at least one of them is 'very close to zero' it is spoken of a ‘QI’ of the non-singlet type. This situation produces an over-valuation of the triplet contributions to the coupling constant, i.e. the FC and SD terms. Thus, these exaggerated values forbids any later analysis at all [9,10]. This phenomena is commonly related to a π-electronic system.

The relationship between HF instabilities and QIs, and a coupling constant calculation at RPA level is straightforward. Following the theory developed in Part I of this work [4], the principal propagator matrix is

$$ {}^{m}\mathbf{P}_{ia,jb} = ({}^{m}\mathbf{A} \pm {}^{m}\mathbf{B})^{-1}_{ia,jb} \tag{1}$$

where $m = 1(3)$ for singlet (triplet) type property and the $+(-)$ sign between ${}^{1}\mathbf{A}({}^{3}\mathbf{A})$ and ${}^{1}\mathbf{B}({}^{3}\mathbf{B})$ is applied. The matrix elements for $\mathbf{A}$ and $\mathbf{B}$ are:

$$\begin{aligned} {}^{1}\mathbf{A}_{ia,jb} &= (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ji} + 2\langle aj|ib\rangle - \langle aj|bi\rangle, \\ {}^{3}\mathbf{A}_{ia,jb} &= (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ji} - \langle aj|bi\rangle, \\ {}^{1}\mathbf{B}_{ia,jb} &= \langle ab|ji\rangle - 2\langle ab|ij\rangle, \qquad {}^{3}\mathbf{B}_{ia,jb} = \langle ab|ji\rangle. \end{aligned} \tag{2}$$

The semiempirical scheme called C(L/C)OPPA (contribution from localized/canonical orbital polarization propagator approach) [11] was developed to allow for the analysis of some linear response molecular properties in terms of ‘local’ contributions, meaning the contribution of individual coupling pathways. They are defined from two occupied (i, j) and two virtual (a, b) MOs.

2.1. Elements of the principal propagator matrix expressed as series

The singlet (${}^{1}\mathbf{P}$) or triplet (${}^{3}\mathbf{P}$) principal propagator matrix can be calculated as a series [12],

$$\begin{aligned} ({}^{m}\mathbf{P}_S)_{ia,jb} &= [\mathbf{E}^{-1}(\mathbf{I} - {}^{m}\mathbf{N}\mathbf{E}^{-1})^{-1}]_{ia,jb} \\ &= \mathbf{E}^{-1}\sum_{i=0}^{\infty}(({}^{m}\mathbf{N}\mathbf{E}^{-1})^{i})_{ia,jb} \\ &\approx \left(\mathbf{E}^{-1}\sum_{n=0}^{p}({}^{m}\mathbf{N}\mathbf{E}^{-1})^{n}\right)_{ia,jb} = ({}^{m}P_S)_{ia,jb;p} \end{aligned} \tag{3}$$

where p stand for the number of terms considered for each series; $\mathbf{E}$ is the diagonal matrix built up from the difference of MOs energies and ${}^{m}\mathbf{N}$ means the two-electronic integrals given in Eq. (2). From now on each matrix element of the matrix obtained as a product between ${}^{m}\mathbf{N}$ and $\mathbf{E}^{-1}$ will be written as

$$ v_{ia,jb} = ({}^{m}\mathbf{N}\mathbf{E}^{-1})_{ia,jb} \tag{4}$$

and the convergence of each series is ensured when

$$ |v_{iajb}| < 1. \tag{5}$$

The maximum value of all $v_{ia,jb}$ will be written as $v^{\max}_{ia,jb}$. The algorithm employed in our code to generate the matrix $\mathbf{P}$ is based on the partial summation

$$ S_n = \sum_{i=0}^{n} X^n \tag{6}$$

X being the matrix that comes from ${}^{m}\mathbf{N}\mathbf{E}^{-1}$; then

$$\begin{aligned} S_1 &= I + X^1 I \\ S_2 &= S_1 + X^2 S_1 \\ S_3 &= S_2 + X^4 S_2 \qquad (7) \\ &\vdots \\ S_n &= S_{n-1} + X^{2n-1} S_{n-1} \qquad (8) \\ &\vdots \end{aligned}$$

In a similar way, it is also possible to generate the $\mathbf{P}$ matrix by splitting it up in two parts, one diagonal, named $\mathbf{P}_d$ and the other one non-diagonal, named $\mathbf{P}_n$ as was done for the generation of the energy matrix $\mathbf{E}_l$ in Ref. [4].

3. Results and discussion

The geometries of all model compounds studied in this work were optimized within the MNDO [13] or AM1 [14] schemes. Calculated values were obtained by applying CLOPPA-(MNDO/AM1)–RPA methods.

3.1. Convergence of each serie

As explained in Part I each element of the series belonging to the inverse matrix of Eq. (3) has a different rate of convergence. This fact depends on how close to one is its corresponding $v_{ia,jb}$. The convergence of the matrix elements corresponding to ${}^{m}\upsilon_{ia,jb}^{\max}$ $(m = 1, 3)$ for the unsaturated compounds CH_2NH and CH_2CH_2, are shown in Figs. 1 and 2. It is observed that the singlet-type propagator elements converge to their RPA values quite fast, i.e. for p less than 10 in Eq. (3) the series is converged for both compounds: CH_2NH with a value of 2.812 (2.836) and C_2H_4 with a value of 2.766 (2.774) for the series (RPA). This means that the highest element of that matrix, i.e. ${}^{1}\upsilon_{ia,jb}^{\max}$, has a value which is by far within the convergence criterion given in Eq. (5). It corresponds to 0.362 for CH_2NH and 0.371 for C_2H_4.

On the other side the triplet-type principal propagator counterparts do need a lot more terms to reach their corresponding RPA values, i.e. more than 30 terms for CH_2NH to reach a value of 19.063 (19.748); and close to 500 terms for C_2H_4 to reach a value of 146.149 (146.191) for the series (RPA). This slow rate of convergence is due to the fact that the highest matrix element is much closer to 1 than in the previous cases. They are 0.885 for CH_2NH and 0.964 for C_2H_4.

3.2. Criteria of convergence vs QIs

In some previous works QI problems were related to the difference HOMO–LUMO [3]. In Fig. 3 the highest element ${}^{3}\upsilon_{ia,jb}^{\max}$ as well as the corresponding HOMO–LUMO differences as a function of the smallest eigenvalue of the principal propagator matrix is given for different kind of model compounds, some are saturated and others are unsaturated. Their nomenclature and ${}^{3}\upsilon_{ia,jb}^{\max}$ values are given in Table 1. In Ref. [9] it was shown that when the smallest eigenvalue is smaller than 0.11 there appears a QI. There is no straightforward relationship between both parameters. On the other side when considering ${}^{3}\upsilon_{ia,jb}^{\max}$ it is easy to find out one minimum value for this parameter that ensure the lower limit for a calculation to be QI for unsaturated compounds. On the left of the dotted line in Fig. 3 all compounds with QI are included. From their values it appears that when unsaturated model compounds have ${}^{3}\upsilon_{ia,jb}^{\max}$ less than 0.75 they will not be affected by QI problems, at least for model compounds which have one pair of π-electrons.

According to the convergence criterion of the power series mentioned in Section 2, each series is convergent when the absolute value of the matrix elements is less than one, i.e.

$$|{}^{1,3}\{NE^{-1}\}_{ia,jb}| < 1.$$

This is an alternative 'mathematical' criterion to determine the threshold for the occurrence of instabilities, e.g. a matrix element with an absolute value equal or larger than 1 will produce instability.

Furthermore, from Fig. 3, it is seen that ${}^{3}\upsilon_{ia,jb}^{\max}$ for the D and E calculations are less than 0.75. They give J values that are over-valued compared with Me_3-$PbPbH_3$ model compounds. It seems that this model compound have a different pattern of eigenvalues that need more studies to be understood. Thus, we propose

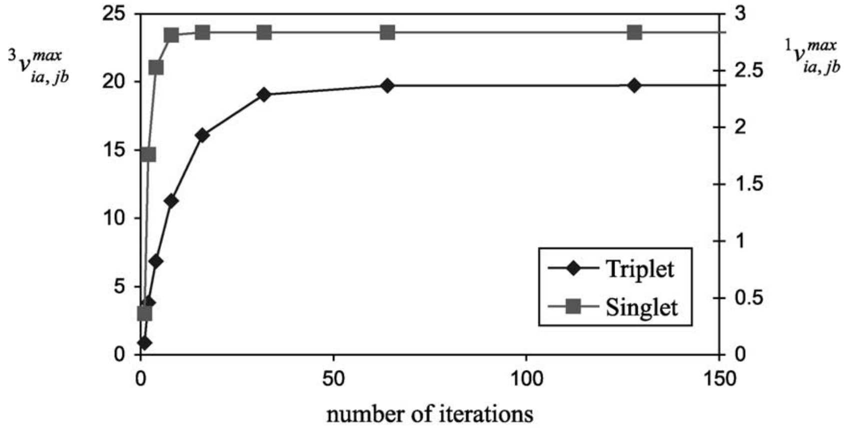


Fig. 1. Triplet and singlet principal propagator behavior for the compound CH_2NH.

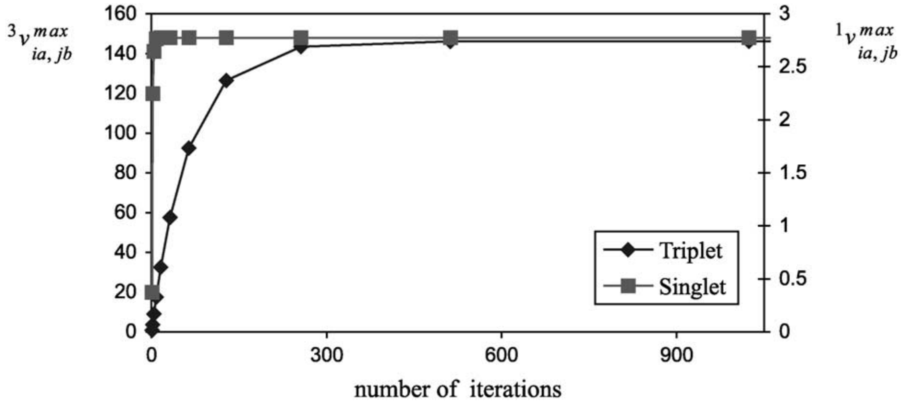
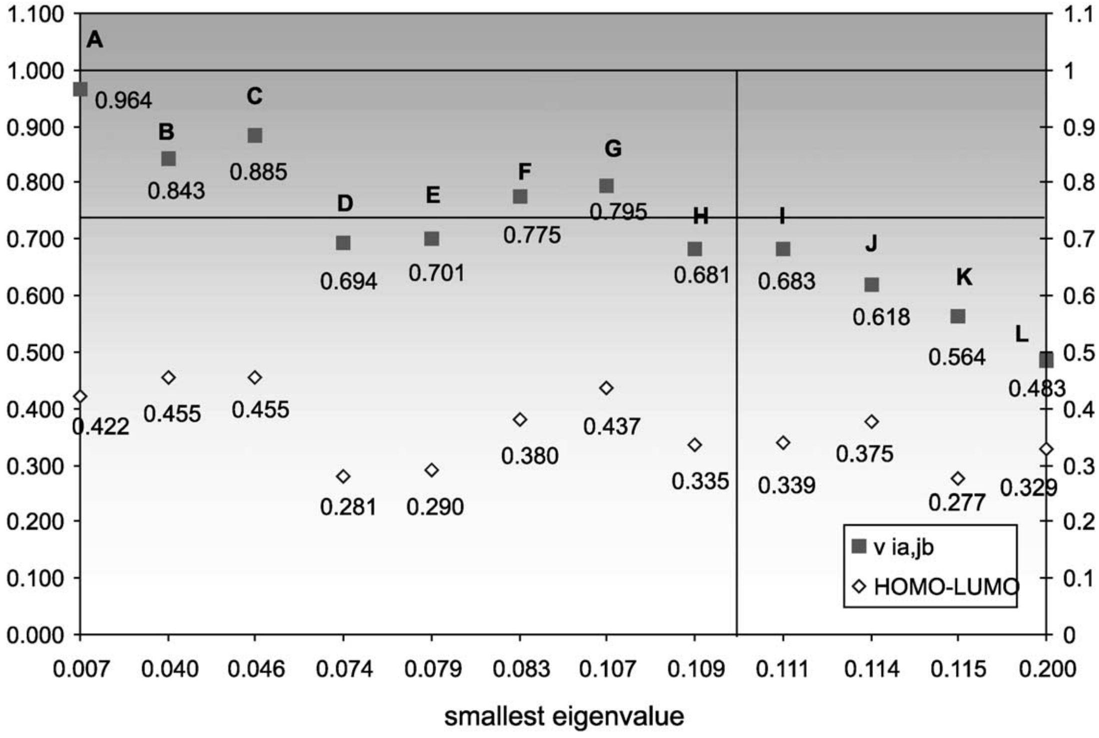


Fig. 2. Triplet and singlet principal propagator behavior for the compound H_2CCH_2.



A	H2CCH2	MNDO	G	H3SnSnH3	MNDO
B	HCCH	MNDO	H	H3SnSnH3	AM1
C	HNCH2	MNDO	I	H3SiSiH3	MNDO
D	H3PbPbH3	MNDO	J	H3CCH3	MNDO
E	H3PbPbH3	MNDO	I	H3SiSiH3	MNDO
F	H3SiSiH3	AM1	F	H3SiSiH3	AM1

Fig. 3. HOMO–LUMO and the relationship $^3\nu^{\max}_{ia,jb}$ for different compounds.

Table 1
The total value of $\upsilon^{\max}_{ia,jb}$ and its contributions for different molecular models

Molecule	Method	#	$\{\langle aj\|bi\rangle E^{-1}\}_{iajb}$	$\{\langle ab\|ji\rangle E^{-1}\}_{iajb}$	$\upsilon^{\max}_{ia,jb}$
C_2H_4	MNDO	A	0.618	0.346	0.964
C_2H_2	MNDO	B	0.547	0.296	0.843
CH_2NH	MNDO	C	0.565	0.320	0.885
Pb_2H_6	MNDO	D	0.453	0.241	0.694
Pb_2H_6	AM1	E	0.456	0.245	0.701
Si_2H_6	AM1	F	0.475	0.300	0.775
CH_2O	MNDO	G	0.512	0.283	0.795
Sn_2H_6	MNDO	H	0.442	0.239	0.681
Sn_2H_6	AM1	I	0.449	0.244	0.683
Si_2H_6	MNDO	J	0.404	0.214	0.618
$Me_3Pb-PbH_3$	MNDO	K	0.406	0.158	0.564
C_2H_6	MNDO	L	0.333	0.150	0.483

as a threshold for the occurrence of QI the arbitrary value of 0.75 for the highest $\upsilon_{ia,jb}$ matrix element, when the model compounds are unsaturated and have one π-electronic framework.

3.3. Minimizing QI effects

The absolute value of $\upsilon_{ia,jb}$ can be divided in two parts, i.e. $\{\langle aj|bi\rangle/(\varepsilon_a - \varepsilon_i)C\}_{ia,jb}$ and $\{\langle ab|ji\rangle/(\varepsilon_a - \varepsilon_i)C\}_{ia,jb}$, where C has a value different than one for localized MOs.

This separation of the matrix elements into two terms is quite convenient in order to decide how to minimize the effects of QIs. Three examples of non-singlet QIs, and the way that they are removed are given in Tables 2–4, where only FC contributions are considered. The three molecules analyzed are unsaturated compounds where the highest propagator matrix element corresponds to the localized coupling pathway $\pi\pi^*\pi\pi^*$. All intramolecular couplings are shown and also compared with their corresponding SOPPA(CCSD) values [15].

Considering the three unsaturated model compounds: C_2H_4, CH_2NH and CH_2O which have $^3\upsilon^{\max}_{ia,jb}$ values in the upper and lower extreme of the range of values that produce QI, it is seen that the $^3\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ for ethylene is by far the largest. When any of the MO integrals, $\langle ab|ji\rangle$ or $\langle aj|bi\rangle$ is removed the matrix elements that correspond to $^3\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ diminish drastically.

For ethylene $^3\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ change two orders of magnitude when we neglect any or both of Coulomb or exchange two-electronic integrals corresponding to the $\pi\pi^*\pi\pi^*$ coupling pathway. In Table 2 it is shown that all couplings are over-valued for the complete RPA calculation. Neglecting any or both integrals

Table 2
The FC contribution to J and $\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ in H_2CCH_2 for different approximations

	$(^3P)_{\pi\pi^*\pi\pi^*}$	$^1J_{C-C}$	$^1J_{C-H}$	$^2J_{C-H}$	$^2J_{H-H}$	*cis*-$^3J_{H-H}$	*trans*-$^3J_{H-H}$
a	146.191	226.040	321.430	−154.332	−131.430	120.294	142.655
b	6.531	34.297	178.051	−10.896	−24.131	12.995	35.356
c	3.734	30.457	175.178	−8.024	−21.983	10.846	33.983
d	2.415	28.646	173.823	−6.669	−20.969	9.833	32.194
SOPPA(CCSD)[a]		76.254	156.288	−1.488	0.399	12.168	18.506

(a) Every term is taken as such. (b) The $\langle ab|ji\rangle$ integral is removed from the problematic matrix element. (c) The $\langle aj|bi\rangle$ integral is removed from the problematic matrix element. (d) Both integrals are removed from the problematic matrix element.

[a] Ref. [13].

Table 3
The FC contribution to J and $\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ in H_2CNH for different approximations

	$(^3P)_{\pi\pi^*\pi\pi^*}$	$^1J_{C-N}$	$^1J_{C-H_1}$	$^1J_{C-H_2}$	$^2J_{N-H_1}$	$^2J_{N-H_2}$	$^2J_{C-H_3}$	$^2J_{H-H}$	*cis*-$^3J_{H-H}$	*trans*-$^3J_{H-H}$
a	19.748	1.157	208.855	192.963	6.157	−4.149	−22.297	1.466	33.155	56.845
b	4.795	6.926	195.258	179.870	2.012	−8.454	−12.416	11.236	26.054	49.471
c	3.039	7.604	193.661	178.332	1.525	−8.961	−11.255	12.384	25.220	48.605
d	2.054	7.984	192.765	177.469	1.252	−9.244	−10.604	13.028	24.752	48.119
SOPPA(CCSD)[a]		−10.140	170.457	160.720	3.456	−10.629	−10.356	16.880	25.007	18.358

(a) Every term is taken as such. (b) The ⟨*ab*|*ji*⟩ integral is removed from the problematic matrix element. (c) The ⟨*aj*|*bi*⟩ integral is removed from the problematic matrix element. (d) Both integrals are removed from the problematic matrix element.

[a] Ref. [13].

Table 4
The FC contribution to J and $\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ in H_2CO for different approximations

	$(^3P)_{\pi\pi^*\pi\pi^*}$	$^1J_{C-O}$	$^1J_{C-O}$	$^2J_{H-H}$	$^2J_{O-H_1}$
a	9.202	15.265	194.826	67.787	0.212
b	3.774	16.720	190.882	70.440	−0.767
c	2.553	17.047	189.995	71.037	−0.987
d	1.824	17.242	189.466	71.393	−1.118
SOPPA(CCSD)[a]		11.173	175.361	41.137	−5.604

(a) Every term is taken as such. (b) The ⟨*ab*|*ji*⟩ integral is removed from the problematic matrix element. (c) The ⟨*aj*|*bi*⟩ integral is removed from the problematic matrix element. (d) Both integrals are removed from the problematic matrix element.

[a] Ref. [13].

Table 5
The FC contribution to J and $\upsilon^{\max}_{\sigma\sigma^*\sigma\sigma^*}$ in Si_2H_6 for different approximations

	Si_2H_6					
	$(^3P)_{\sigma\sigma^*\sigma\sigma^*}$	$^1J_{Si-Si}$	$^1J_{Si-H}$	$^2J_{Si-H}$	$^2J_{H-H}$	$^3J_{H-H}$
a	11.084	314.959	−438.807	61.378	−94.301	31.864
b	4.634	125.854	−405.594	28.195	−88.461	26.012
c	3.407	89.890	−399.277	21.918	−87.350	24.897
d	2.386	59.954	−394.019	16.654	−86.426	23.971

(a) Every term is taken as such. (b) The ⟨*ab*|*ji*⟩ integral is removed from the problematic matrix element. (c) The ⟨*aj*|*bi*⟩ integral is removed from the problematic matrix element. (d) Both integrals are removed from the problematic matrix element.

mentioned above it reduce the couplings in such a way that most of them becomes closer to a SOPPA(CCSD) calculation. There are still three cases where the new values do not become as close to SOPPA(CCSD) values as the others: the one-bond C–C, the geminal C–H and the vicinal *trans* H–H couplings, which could mean that in these cases $\pi\pi^*$ excitation is very important.

As shown in Tables 3 and 4 the situation is less dramatic. The $^3\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ is not very high as in the previous case. When we neglect any of Coulomb or exchange two-electronic integrals all RPA coupling values are modified in such a way that they become close to SOPPA(CCSD) values with the exception of one-bond C–N, the geminal H–H coupling in CH_2O and the vicinal *trans* H–H couplings. For the model compound CH_2NH the vicinal *cis* H–H coupling is very well reproduced as is also observed for ethylene. Geminal couplings are modified giving values with a difference of 2 Hz or less for CH_2NH.

The use of option c with respect to b makes a difference that is almost twice the modification between options d and c, as seen from Tables 2–4. The value of $^3\upsilon^{\max}_{\pi\pi^*\pi\pi^*}$ is such that it obeys the following relationship

$$H_2CCH_2 > CH_2NH > CH_2O.$$

In this way the one-bond C–X coupling is slightly modified for $X = O$ and largely modified for $X = CH_2$ when options b–d are applied. Three points corresponding to saturated model compounds are at the left of Fig. 3. The AM1 calculation for H_3SiSiH_3 gives an attenuated QI: its $^3\upsilon^{\max}_{ia,jb}$ is close to 0.75. When Coulomb or exchange integrals are removed from that term the J(Si–Si) becomes closer to its MNDO value, which is stable as shown in Table 5. The indirect nuclear spin coupling for the H_3PbPbH_3 molecule do need more analysis in order to understand its behavior.

4. Concluding remarks

Making use of few mathematical basic concepts we are able to tackle one of the most frequent problems encountered in calculations of some molecular properties like the indirect nuclear spin–spin coupling constant at RPA level, i.e. instabilities and QIs. Analyzing the highest matrix element ${}^3v_{ia,jb}$, it is possible to know beforehand in which situation the compound is; for instance: stable, quasi-instable or instable. In cases where the molecular ground state wavefunction presents non-singlet Hartree–Fock QIs we should expect a much slower convergence for each series corresponding to each element of the principal propagator though at different rate depending on the coupling pathway.

For some saturated model compounds we found also QIs like, for instance H_3XXH_3, $X = Si$ calculated with AM1 wavefunction and $X = Pb$ calculated with both semiempirical wavefunctions. The other similar model compounds with $X = C$ and Sn do not have QI problems. In case of H_3PbPbH_3 the localized bond Pb–Pb have a different electronic density structure with respect to the other H_3XXH_3 model compounds. Their electronic density obtained from MNDO and AM1 semiempirical schemes is lower in the middle of the bond than in the region close to the Pb atoms.

We have shown that our previous criterion used to establish when a QI problem should appear (i.e. when the lowest eigenvalue of the principal propagator is lower than 0.11) is equivalent to that given here, i.e. the ${}^3v_{ia,jb}^{\max}$ should be larger than 0.75.

Our scheme for obtaining the principal propagator matrix as a series gives us the opportunity to find out ‘where’ exactly the problem is generated within the matrix. As a corollary to the previous statement, this scheme gives us enough information about how a certain coupling pathway is influencing or disturbing each coupling constant for the molecule studied. Hence, for the unsaturated compounds analyzed here we found that the QI is due to the $\pi\pi^*\pi\pi^*$ coupling pathway. In order to avoid that QI problems one needs to neglect the Coulomb or exchange integrals from that specific element of the principal propagator matrix. Minimizing the origin of the QI problems is then possible to closely predict the best theoretical results for couplings other than those mainly influenced by the $\pi\pi^*$ excitation. This gives the way to work with CLOPPA scheme on large molecules which contain π-like bonds. Work on this line is being done in our Lab.

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References

[1] R.H. Contreras, J.E. Peralta, C.G. Giribet, M.C. Ruiz de Azúa, J. Facelli, Annu. Rep. NMR Spectrosc. 41 (2000) 55.
[2] T. Helgaker, M. Jaszunski, K. Ruud, Chem. Rev. 99 (1999) 293.
[3] R.H. Contreras, M.C. Ruiz de Azúa, C.G. Giribet, G.A. Aucar, R. Lobayan de Bonckzok, J. Mol. Struct. (Theochem) 249 (1993) 284.
[4] C.A. Gomez, P.F. Provasi, G.A. Aucar, J. Mol. Struct. (Theochem) 584 (2002) 159.
[5] J.A. Pople, J.W. McIver, N.S. Ostlund, Chem. Phys. Lett. 1 (1967) 465.
[6] A.C. Blizzard, D.P. Santry, J. Chem. Phys. 55 (1971) 950.
[7] A.C. Blizzard, D.P. Santry, J. Chem. Phys. 58 (1973) 4714.
[8] R.H. Contreras, M.A. Natiello, G.E. Scuseria, Magn. Reson. Rev. 9 (1985) 239.
[9] R.M. Lobayan, G.A. Aucar, J. Mol. Struct. (Theochem))452 (1998) 13.
[10] R.M. Lobayan, G.A. Aucar, J. Mol. Struct. (Theochem) 452 (1998) 1.
[11] A.C. Diz, C.G. Giribet, M.C. Ruiz de Azúa, R.H. Contreras, Int. J. Quantum Chem. 663 (1990) 37.
[12] G.A. Aucar, PhD thesis, University of Buenos Aires, 1991.
[13] M.J.S. Dewar, W. Thiel, J. Am. Chem. Soc. 99 (1981) 4899.
[14] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 3902 (1985) 107.
[15] P.F. Provasi, G.A. Aucar, S.P.A. Sauer, J. Chem. Phys. 115 (2001) 1324.