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Order-by-order intermediate Hamiltonian expansions: applications to *ab initio* molecular calculations

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Abstract . — A simple third-order intermediate Hamiltonian method based on the level shift technique is presented and applied to *ab initio* calculations on low-lying electronic states of CH^+ , CH_2^+ and CH_2 . The method is shown to provide a good approximation to full CI for both total energies and excitation energies. Numerous intruder states did not give rise to any instability problems. Series resummation using modified operator [2/1] Padé approximants and deviations of solutions by the present method from the strict size consistency are discussed.

1. Introduction.

Quasidegenerate perturbation theory (QDPT) is recognized to be a powerful method in quantum chemistry. It provides both efficient tools for *ab initio* calculations of open-shell molecular systems and a general theory of effective valence-shell operators appearing in semiempirical models of electronic structure [1, 2]. Unfortunately, straightforward applications of conventional Bloch-Brandow effective Hamiltonian QDPT [3, 4] to highly degenerate systems as well as to the complete-valence-space effective Hamiltonian problem are often blocked by convergence difficulties in the presence of intruder states [1, 5]. Those difficulties stem from the way the Bloch-Brandow effective Hamiltonians are defined and apparently cannot be completely avoided by resummation techniques or by simple modifications of zero-order approximations [6].

The intermediate Hamiltonian approach of Malrieu *et al.* [7] seems to provide a rather general solution to the intruder state problem via relaxing the requirements imposed on several “intermediate” eigenstates of an effective Hamiltonian. Over the last few years a wide variety of intermediate Hamiltonian QDPT methods have been described [8-16]. Despite the formal progress, these methods have not received many applications in computational chemistry, except for simple second-order schemes ([8, 9, 16, 17] and Refs. therein).

In the previous paper [18] we have formulated a general and physically transparent method of constructing order-by-order intermediate Hamiltonian expansions based on the intermediate level shift technique [10, 11, 13, 19]. Designed to inspect various intermediate Hamiltonian formalisms from an unified point of view and being important for better understanding of theoretical foundations of intermediate Hamiltonians, this approach can also give rise to a practically valuable tool for *ab initio* calculations of open-shell systems. It should combine the major advantages of the previously described perturbation-iteration shift method [13] (efficient elimination of intruders without any modification of zero-order approximations, semiquantitative description of low-lying “intermediate” states) with the computational simplicity of conventional order-by-order QDPT procedures [2, 20]. While our formulation is not strictly size-consistent, deviations from size consistency are expected to be small [13] and should not be of critical importance for most applications in quantum chemistry.

In the present work we explore the performance of the third order computational scheme based on our intermediate Hamiltonian QDPT formulation. Two alternative ways to define zero-order Hamiltonians are used, namely, the “model” scheme of Møller and Plesset (MP) [21] and the Epstein-Nesbet (EN) partitioning [22]. The set of molecules studied in this work (CH^+ , CH_2^+ , CH_2) is chosen in order to enable the comparison of the QDPT results for several low-lying states and transition energies with the corresponding full CI data [23, 24] for reliable (at least of double zeta plus polarization quality) basis sets. We restrict our attention to so-called valence states and employ model spaces spanned only by valence-type configurations, thus tempting to solve the famous problem of constructing valence-shell Hamiltonians from the first principles [25]. We also study the possibility of rectifying truncation errors using our adaptation [26] of the operator Padé resummation method [27, 28]. Finally, we estimate the size-consistency errors of our scheme via energy computation for a supersystem comprising two non-interacting molecules.

The outline of the paper is the following: section 2 provides a brief review of the theory which is discussed in details elsewhere [18, 26] and presents the derivation of main working formulae. In section 3 we describe the numerical experiment and discuss the results of calculations. The final section contains the concluding remarks.

2. Theory.

2.1 ORDER-BY-ORDER INTERMEDIATE HAMILTONIAN EXPANSIONS. — Assume that we are interested in M eigensolutions of a stationary Schrödinger equation

$$H | \psi_m \rangle = E_m | \psi_m \rangle, \quad m = 1, \dots, M \quad (1)$$

We start as usual by partitioning the Hamiltonian H into the zero-order part H_0 and the perturbation $V = H - H_0$. The solutions of the zero-order problem

$$H_0 | k \rangle = \varepsilon_k | k \rangle \quad (2)$$

are supposed to be known. The total Hilbert space L is split into two subspaces, the (extended) model space L_P with the projector P and the outer space L_Q projected by $Q = 1 - P$. The model space is assumed to be spanned by an appropriate set of zero-order eigenvectors; $\dim L_P > M$. We search for an intermediate Hamiltonian \tilde{H} [7] acting within L_P and describing properly $M < \dim L_P$ target eigenstates of H . The associated wave-like operator $R : R = P + QR$

connected with \tilde{H} by the relation

$$\tilde{H} = PHR \tag{3}$$

should obey the conditions

$$RP | \psi_m \rangle = | \psi_m \rangle, \quad m = 1, \dots, M \tag{4}$$

Equations (3, 4) imply that M eigenstates of \tilde{H} should coincide with the model space projections of the corresponding target solutions of equation (1). Introducing the orthogonal projector \mathcal{P} onto the subspace spanned by these eigenvectors $\{ | P\psi_m \rangle \}$, $m = 1, \dots, M$, one can write down the Bloch-like equation for RP [10, 11, 13]:

$$Q [R, H_0] \mathcal{P} = Q(VR - RVR)\mathcal{P} \tag{5}$$

This equation imposes no restriction on the R component which acts upon the $(\dim L_P - M)$ -dimensional subspace projected by $P - \mathcal{P}$. Various versions of the intermediate Hamiltonian theory differ essentially in the way of defining $R(P - \mathcal{P})$. To specify the entire R operator by an equation suitable for Rayleigh - Schrödinger QDPT treatment, it is convenient to subdivide L_P into the main model space L_M and the intermediate space L_I projected by the operators $P_M = \lim_{V \rightarrow 0} \mathcal{P}$ and $P_I = P - P_M$ respectively. In what follows, we shall use the notation $\varepsilon_m, | m \rangle$ for zero-order solutions spanning the main model space; $\varepsilon_i, | i \rangle$ and $\varepsilon_\alpha, | \alpha \rangle$ will denote zero-order solutions belonging respectively to the intermediate space and the outer space.

The present version of the intermediate level shift technique [18] derives the wave-like operator from the shifted Bloch equation

$$Q [R, (H_0 + S)] P = Q(VR - RVR)P + QRS (P - P_M) \tag{6}$$

where $S = P_I S P_I$ is the shift operator acting in the intermediate space. The compatibility of equation (6) with the fundamental equation (5) for arbitrary shift is easily verified. Here we adopt the diagonal form of S :

$$S = \sum_i | i \rangle S_i \langle i | \tag{7}$$

where $\{s_i\}$ are fixed real numbers. The proper choice of shift parameters s_i should prevent the appearance of small energy differences in the shifted Liouvillian

$$\begin{aligned} Q [R, (H_0 + S)] P = & \sum_m \sum_\alpha | \alpha \rangle (\varepsilon_m - \varepsilon_\alpha) \langle \alpha | R | m \rangle \langle m | \\ & + \sum_i \sum_\alpha | \alpha \rangle (\varepsilon_i + s_i - \varepsilon_\alpha) \langle \alpha | R | i \rangle \langle i | \end{aligned} \tag{8}$$

Expanding equation (6) order by order, one arrives at the recursion formula

$$\begin{aligned} & Q [R^{(n)}, (H_0 + S)] P = \\ = & Q \left(VR^{(n-1)} - \sum_{k=1}^{n-1} \left(R^{(k)} VR^{(n-k-1)} - R^{(k)} S \mathcal{P}^{(n-k)} \right) \right) P \end{aligned} \tag{9}$$

where the superscripts indicate the order in perturbation. Equations (9) and (3) yield the desired QDPT series for R and \tilde{H} provided the expansion for \mathcal{P} is known. As it has been shown in reference [18], this expansion is readily derived from the auxiliary Bloch waveoperator associated with the main model space.

One is always able to partition the Hilbert space in such a way that the $P_M H_0 P_M$ and $Q H_0 Q$ spectra are well separated in energy; possible quasidegeneracies between L_I - and L_Q -space zero-order states are avoided by putting

$$s_i = \bar{\varepsilon} - \varepsilon_i, \quad \bar{\varepsilon} = \max(\{\varepsilon_m\}), \quad (10)$$

i.e. by lifting all the intermediate zero-order levels to the upper main level. As has been shown earlier [18], this choice gives rise to stable QDPT expansions, avoiding ill-defined terms in the intermediate Hamiltonian up to third order inclusively. Moreover, in the case of exact degeneracy between the upper main zero-order level and the lowest intermediate level the corresponding shift component disappears, thus offering a remarkable possibility of adequately describing avoided crossings between target and intermediate levels [13].

Introducing the shifted resolvent

$$\bar{G}[A] = \sum_m \frac{Q}{\varepsilon_m - H_0} A |m\rangle\langle m| + \frac{Q}{\bar{\varepsilon} - H_0} A P_I \quad (11)$$

and taking into account that

$$S\mathcal{P}^{(1)} = \sum_{i,m} \frac{|i\rangle\langle s_i| V |m\rangle\langle m|}{\varepsilon_m - \varepsilon_i} \quad (12)$$

[18], we can write down explicit formulae for low-order terms in the wave-like operator expansion:

$$R^{(1)} = \bar{G}[VP] \quad (13)$$

$$\begin{aligned} R^{(2)} &= \bar{G} [VR^{(1)} - R^{(1)}VP + R^{(1)}S\mathcal{P}^{(1)}] \\ &= \bar{G} [V\bar{G}[VP]] - \bar{G} [\bar{G}[VP]W] \end{aligned} \quad (14)$$

where the operator $W \equiv PVP - S\mathcal{P}^{(1)}$ differs from PVP only by its $P_I \div P_M$ block:

$$\langle i|W|m\rangle = \frac{\varepsilon_m - \bar{\varepsilon}}{\varepsilon_m - \varepsilon_i} \langle i|V|m\rangle \quad (15)$$

The corresponding third order expression for the intermediate Hamiltonian is immediately obtained from equations (13, 14) and (3).

Note that the scaling factors in equation (15) cannot exceed 1, i.e. the level shift does not cause any increase of numerators in $R^{(2)}$ and $\tilde{H}^{(3)}$

The expressions (13, 14) formally resemble those appearing in conventional shifted-denominator effective Hamiltonian QDPT ([2, 20] and Refs. therein). Therefore one can make use of efficient third-order computational strategies [20] (except for those which explicitly take into account the cancellations of unlinked terms). The formal similarity should not mask the essential difference between the present approach and the level shift technique used in effective Hamiltonian QDPT. In the latter case the shift is introduced in order to construct the series expansion of the same operator about a different point while in the former case it changes the

operator to be expanded. Being hidden at the second-order level [1, 7], this difference manifests itself in the third order calculations, as discussed in details in reference [18].

It should be pointed out that the present formulation does not impose strict degeneracy on the main model space (cf. [7]). This feature is important for simultaneous treatment of molecular electronic states which substantially differ in energy.

2.2 OPERATOR PADÉ APPROXIMANTS. — The $[N+1/N]$ and $[N/N]$ Padé approximants are widely used to improve the convergence of non-degenerate perturbation theory series [29]. The extension of this technique to QDPT is not straightforward since the methods of this group do not yield power series for energy eigenvalues.

Several authors [20, 30-34] have applied Padé approximants to extrapolate the sequences of effective Hamiltonian eigenvalues; however, this approach meets with conceptual difficulties in assigning the order-by-order eigenvalues to specific sequences. This difficulty is easily avoided by using the operator (matrix) Padé approximants to directly resum the effective Hamiltonian series [28]; unfortunately, the results of recent numerical experiments ([33] and Refs. therein, [26]) were disappointing. This failure might be explained by rapid divergency (in conventional effective Hamiltonian theory) or rather slow convergency (in intermediate Hamiltonian theory) of upper eigenstates which are usually of no interest *per se* but which necessarily enter the operator Padé approximant. To circumvent this problem, we use the operator Padé approximation to resum the power expansion of the operator

$$\mathcal{P}\tilde{H}(\lambda)\mathcal{P} = \mathcal{P}H_0\mathcal{P} + \lambda\mathcal{P}\tilde{H}^{(1)}\mathcal{P} + \lambda^2\mathcal{P}\tilde{H}^{(2)}\mathcal{P} + ..$$

where \mathcal{P} is assumed to be fixed at its physically meaningful ($\lambda = 1$) value. The projected intermediate Hamiltonian $\mathcal{P}\tilde{H}\mathcal{P}$ is essentially the generalized effective Hamiltonian recently introduced by Evangelisti *et al.* [35]. Its right eigenstates coincide with the main eigenstates of \tilde{H} while the intermediate ones are cut by the projection. The unknown exact projector \mathcal{P} should be replaced by its approximant deduced from eigenvectors of the best available finite-order intermediate Hamiltonian. This version of Padé approximation technique is discussed in details elsewhere [26].

3. Results and discussion.

To study the performance of the present approach in molecular ground and excited state calculations, we applied it to compute low-lying singlet states of the CH^+ molecular ion, four lowest $^2\text{A}_1$ states of CH_2^+ and two lowest $^1\text{A}_1$ states of neutral CH_2 . In the latter case several geometries were considered. This section provides a detailed comparison of our second- and third order results with the corresponding full CI (i.e. exact for the chosen orbital bases) data. We also describe numerical investigations of non-additivity effects in intermediate Hamiltonian QDPT calculations on a supersystem comprising two non-interacting Li_2 molecules.

3.1 CH^+ . — In the CH^+ calculations we used the split valence plus diffuse plus polarization contracted Gaussian basis set taken from the full CI calculations of Olsen *et al.* [23]. This basis enables to describe reasonably both ground and low-lying excited electronic states. The internuclear separation was fixed at $r = 2.13713$ a.u. One-electron functions and orbital energies were generated by solving the simplified fractional-occupancy restricted SCF equations for the $1\sigma^2 2\sigma^2 3\sigma$ configuration of CH^{2+} . The extended model space comprised all possible symmetry-allowed distributions of four valence electrons within the valence orbital space spanned by 2σ ,

3σ , 4σ and 1π MO's. With this partitioning of the Hilbert space, the spread of zero-order model levels exceeded 3 a.u. for the MP Hamiltonian breakup and approached 2 a.u. within the EN scheme, thus causing strong overlapping of the PH_0P and QH_0Q spectra. The main model space was spanned by several lowest unperturbed model states in such a way that the separation of $P_M H_0 P_M$ and $Q H_0 Q$ spectra was guaranteed. With this constraint, we could search for three $1^1\Sigma^+$, one $1^1\Pi$ and one $1^1\Delta$ "main" eigensolutions. For the sake of comparison we also performed standard (non-shifted) effective Hamiltonian QDPT calculations.

Computed total energy values for main \tilde{H} eigenstates are listed in table I. The presence of numerous intruder states caused a strong divergency of the conventional effective Hamiltonian QDPT (EH QDPT) series which manifested itself in third order (notice that restricted to second order, this expansion yielded quite reasonable energy estimates). In contrast, our third-order intermediate Hamiltonian scheme (IH QDPT) reproduced "exact" total energies to within a few *mhartree* both with MP and EN breakup of H . In passing from second to third order the deviation of intermediate Hamiltonian eigenvalues from the corresponding full CI energies decreased systematically; the third order corrections were of particular importance when the EN zero-order approximation was used. The operator $[2/1]$ Padé approximant provided a significant improvement over the third order result only within the EN scheme.

Table I. — *Calculated total energies (a.u., relative to full CI) for low-lying electronic states of CH⁺*

Method	$1^1\Sigma^+$	$2^1\Sigma^+$	$3^1\Sigma^+$	$1^1\Pi$	$1^1\Delta$	Mean absolute error
Full CI [23]	-38.01964	-37.70546	-37.52262	-37.90095	-37.76371	
EH QDPT:						
MP, 2nd order	0.01754	0.00744	-0.00277	0.00340	0.00714	0.00766
MP, 3rd order	0.06321	-0.04032	0.08061	-0.01861	0.03313	0.04717
EN, 2nd order	0.01261	-0.00750	-0.04021	-0.00803	-0.01699	0.01907
EN, 3rd order	-0.06058	*	*	*	0.03903	*
IH QDPT:						
MP, 2nd order	0.01238	0.00184	-0.00331	0.00920	0.00515	0.00638
MP, 3rd order	0.00240	0.00280	0.00621	0.00181	0.00128	0.00290
MP, [2/1] Pade	0.00086	0.00296	0.00540	0.00110	0.00109	0.00228
EN, 2nd order	-0.00912	-0.00852	-0.01803	-0.01003	-0.01035	0.01221
EN, 3rd order	0.00185	0.00272	-0.00909	0.00226	0.00189	0.00356
EN, [2/1] Pade	0.00069	0.00151	0.00481	0.00098	0.00055	0.00171

(*) complex eigenvalues of the effective Hamiltonian

The third order corrections were typically 7-10 times smaller than those in second order. This feature along with the rapid approaching the full CI limit indicates a "practical convergency" of our perturbation expansion.

Table II. — *Calculated vertical excitation energies for CH⁺ (eV).*

Method	Final state				Mean absolute error
	2 ¹ Σ ⁺	3 ¹ Σ ⁺	1 ¹ Π	1 ¹ Δ	
Full CI [23]	8.549	13.525	3.230	6.964	
IH QDPT:					
MP, 2nd order	8.263	13.098	3.143	6.768	0.249
MP, 3rd order	8.556	13.628	3.214	6.934	0.039
MP, [2/1] Padé	8.606	13.648	3.236	6.971	0.048
EN, 2nd order	8.566	13.142	3.205	6.931	0.114
EN, 3rd order	8.573	13.753	3.241	6.965	0.066
EN, [2/1] Padé	8.572	13.637	3.237	6.961	0.037

For various applications it is more important to reproduce accurately energy differences associated with certain physical processes than total energies. Table II presents vertical excitation energies deduced from intermediate Hamiltonian eigenvalues. As well as for total energies, third order calculations provided a systematic improvement over second order for both zero-order approximations employed in our work. The agreement between third-order and full CI excitation energies was usually better than 0.1 eV. A further reduction of errors was gained via Padé resummation.

Finally, it is interesting to note that the excitation energies derived from [2/1] Padé approximants showed little dependence on the choice of H_0 . The average absolute difference between MP and EN results was only 0.014, going down by a factor of 3 with respect to the corresponding third order difference.

3.2 CH₂⁺. — Our computations on CH₂⁺ used the same double zeta plus polarization basis set and the equilibrium geometry of the neutral CH₂ molecule ($r(\text{C-H}) = 2.11$ a.u., $\widehat{\text{HCH}} = 102.4^\circ$) as in the full CI calculations of Bauschlicher and Taylor [24]. To ensure a roughly balanced description of several lowest ²A₁ states, the zero-order Hamiltonians were built of self-consistent MO's corresponding to the 1a₁² 2a₁ 3a₁ 1b₁ 1b₂ configuration of CH₂²⁺. As well as in the benchmark full CI calculations, the 1a₁ orbital was frozen at the correlation step. The complete valence space should be spanned by all possible distributions of five electrons among the valence orbitals 2a₁, 3a₁, 4a₁, 1b₁, 1b₂ and 2b₂. To reduce the size of the problem, we omitted the valence determinants with negligible weights in five lowest ²A₁ solutions for

the full valence CI problem; the resulting model space comprised 25 determinants of the A_1 symmetry. With this restricted valence space, the spread of zero-order model levels still was wide; the intruder state problem remained and ruined the convergence of the non-shifted series. The choice of the main model space according to the $P_M H_0 P_M - Q H_0 Q$ separation criterion allowed to search for four 2A_1 "main" states.

The results of our calculations along with the valence Hamiltonian QDPT data of Wang and Freed [34] are collected in tables III and IV. The intermediate-Hamiltonian QDPT energy estimates appeared to rapidly converge to their full CI limits for all target states. In the case of MP partitioning, third order total energies were within 0.2–1.2 mhartree of the corresponding full CI values. The order-by-order results from EN calculations were somewhat worse but the errors were successfully rectified by applying the [2/1] Padé resummation.

Table III. — *Calculated total energies (a.u., relative to full CI) for low-lying 2A_1 states of CH_2^+ .*

Method	1^2A_1	2^2A_1	3^2A_1	4^2A_1	Mean absolute error
Full CI [24]	-38.65031	-38.21359	-38.17007	-38.14301	
IH QDPT:					
MP, 2nd order	0.00236	0.00313	0.00142	0.00245	0.00234
MP, 3rd order	0.00026	0.00058	0.00122	0.00060	0.00067
MP, [2/1] Pade	0.00021	0.00050	0.00120	0.00054	0.00061
EN, 2nd order	-0.01270	-0.01881	-0.02423	-0.02235	0.01952
EN, 3rd order	0.00142	0.00305	0.00680	0.00547	0.00419
EN, [2/1] Pade	-0.00014	0.00002	0.00123	0.00117	0.00064
EH QDPT [34]:					
MP*, 2nd order	-0.0357	-0.0234	-0.0275	-0.0230	0.0274
MP*, 3rd order	0.0512	-0.1570	-0.0468	-0.0346	0.0724

(*) SCF valence orbital energies were shifted to their average value

The agreement between intermediate-Hamiltonian QDPT and full CI $1^2A_1 - n^2A_1$ transition energies for CH_2^+ (Tab. IV) was slightly better than that for CH^+ . Notice that the MP second order energy differences were so accurate that the third-order calculations did not exhibit any improvement. In contrast, third order terms (as well as higher order corrections as estimated by the Padé approximation) were found to be important for deriving energy

Table IV. — *Calculated vertical excitation energies for CH₂⁺ (eV).*

Method	Final state			Mean absolute error
	2 ² A ₁	3 ² A ₁	4 ² A ₁	
Full CI [24]	11.885	13.068	13.805	
IH QDPT:				
MP, 2nd order	11.906	13.043	13.807	0.016
MP, 3rd order	11.894	13.094	13.813	0.015
MP, [2/1] Pade	11.893	13.095	13.814	0.015
EN, 2nd order	11.718	12.754	13.542	0.215
EN, 3rd order	11.930	13.215	13.915	0.101
EN, [2/1] Pade	11.888	13.107	13.840	0.026
EH QDPT [34]:				
MP*, 2nd order	12.22	13.28	14.15	0.30
MP*, 3rd order	6.22	10.40	11.41	3.58

(*) Same as in Table III

differences from the EN-type scheme.

Now let us compare our results with those obtained in the frames of the conventional effective Hamiltonian QDPT by Wang and Freed [34]. In the latter case, the MP definition of H_0 has been modified *via* averaging valence orbital energies. Although this modification formally avoided the intruders, a dramatic increase of errors in passing from second to third order seems to be a manifestation of the divergence of the effective Hamiltonian expansion. This effect might be a consequence of the introducing of an additional (level-shifting) diagonal perturbation which first appears in third order terms.

3.3 CH₂. — We performed the third-order calculations for two lowest ¹A₁ states of CH₂ for three different geometries which were the same as in the work of Bauschlicher and Taylor:

i) equilibrium geometry ($r(\text{C—H}) = 2.11$ a.u., $\widehat{\text{HCH}} = 102.4^\circ$);
 ii) the angle was unchanged, the bond length was stretched to 1.5 times the equilibrium;
 iii) $r(\text{C—H}) = 2.11$ a.u., the HCH angle was opened to 170° . To construct the zero-order approximations, the solutions of SCF equations for the ionic configuration $1a_1^2 2a_1^2 3a_1 1b_1 1b_2$ were used. As well as for CH₂⁺, our extended model space was spanned by a subset of valence space determinants and comprised 20 functions with non-negligible contributions to ¹A₁ and ²¹A₁ states for at least one of the three geometries mentioned above. Our results are summarized in tables V and VI. The valence effective Hamiltonian QDPT data [34] are given for

Table V. — Total energy estimates (a.u., relative to full CI) for two lowest $1A_1$ states of CH_2 .

Method	Geometry					
	(i)		(ii)		(iii)	
	1^1A_1	2^1A_1	1^1A_1	2^1A_1	1^1A_1	2^1A_1
Full CI [24]	-39.02714	-38.85828	-38.89924	-38.73570	-38.97928	-38.94000
IH QDPT:						
MP, 2nd order	0.00743	0.00445	0.01253	0.01277	0.00849	0.00748
MP, 3rd order	0.00202	0.00180	0.00522	0.00966	0.00151	0.00130
MP, [2/1] Padé	0.00180	0.00176	0.00470	0.00846	0.00111	0.00100
EN, 2nd order	-0.02841	-0.05194	-0.02691	-0.05068	-0.02910	-0.02983
EN, 3rd order	0.00904	0.01809	0.00661	0.02402	0.00879	0.00958
EN, [2/1] Padé	0.00262	0.00138	0.00146	0.00889	0.00189	0.00227
EH QDPT [34]						
MP [*] , 2nd order	-0.03742	-0.03229	-0.02490	-0.01951	-0.03997	-0.03488
MP [*] , 3rd order	-0.04897					

(*) Same as in Table III.

comparison.

The general trends observed in total and excitation energy estimates for the geometries i) and iii) were essentially the same as for previous examples. As for the stretched geometry ii), the total energies seemed to be fairly convergent but the rate of approaching the full CI limit for the upper state was relatively low. The difference in convergence rate for the two states resulted in worsening the MP transition energy in passing from second to third order. This effect should be explained by strong inadequacy of the restricted-SCF-based valence space in the region of bond breaking and apparently might be avoided by employing MCSCF one-electron functions.

The third-order MP scheme with subsequent operator [2/1] Padé resummation yielded the i) → ii) deformation energy with ca.2 % error. The corresponding result obtained with EN partitioning was even better. This level of accuracy seems to be nontrivial for the complicated problem of simultaneous breaking of two chemical bonds. The discrepancies between third-order and full CI i) → iii) bending energies were negligible. These results indicate the applicability of the present approach to potential energy surface calculations.

3.4 TWO NON-INTERACTING Li_2 MOLECULES. — To study the size-consistency of our calculation scheme, we applied it to the ground state of the supersystem composed of two non-interacting (separated by a distance ca. 200 a.u.) Li_2 molecules and compared the resulting energy ($E(2Li_2)$) with that obtained for a single molecule ($E(Li_2)$). The deviation from size consistency was characterized by the quantity $\frac{1}{2}E(2Li_2) - E(Li_2)$ which should be zero for size consistent approaches.

We employed the (9s4p)/[4s2p] Huzinaga - Dunning contracted Gaussian basis set [36, 37].

Table VI. — *Calculated energy differences for CH₂.*

Method	1^1A_1 deformation energy,		$1^1A_1-2^1A_1$ excitation energy,		
	a.u.		eV		
	(i)→(ii)	(i)→(iii)	(i)	(ii)	(iii)
Full CI [24]	0.12790	0.04786	4.60	4.45	1.07
IH QDPT:					
MP, 2nd order	0.13300	0.04893	4.514	4.457	1.041
MP, 3rd order	0.13109	0.04735	4.602	4.544	1.063
MP, [2/1] Pade	0.13080	0.04718	4.594	4.553	1.066
EN, 2nd order	0.12943	0.04721	3.956	3.806	1.049
EN, 3rd order	0.12547	0.04761	4.842	4.924	1.090
EN, [2/1] Pade	0.12693	0.04713	4.567	4.650	1.079
EH QDPT [34]					
MP [*] , 2nd order	0.14042	0.04531	4.73	4.60	1.21

(*) Same as in Table III

One-electron functions and orbital energies were found by solving the SCF problem for Li_2^+ ($1\sigma_g^2 1\sigma_u^2 2\sigma_g$). The extended model spaces for Li_2 and $2(Li_2)$ were defined in a consistent way by allowing all possible excitations within the valence orbital subspace (σ_g, σ_u^*). The main model space was assumed to be one-dimensional with doubly occupied bonding orbital(s). Although both the extended model space and main model space were complete, the explicit non-separability of the shift [19] precluded from the exact additivity of energy estimates. The calculations were carried out for two values of Li_2 bond length: equilibrium ($r = 5.05$ a.u.) and stretched ($r = 8$ a.u.). At the equilibrium geometry, the ground state wavefunction is dominated by its main model space component, while the distorted molecule provides an example of strong coupling between the main model space and the intermediate space. The results are listed in table VII. For the sake of comparison, we also estimated the non-additivity of energy values obtained from the single reference (SR) and multireference (MR) SDCI methods. In the latter case, the reference set comprised all basis determinants of the extended model space.

At the equilibrium geometry, size-inconsistency error from our third order MP intermediate Hamiltonian QDPT was remarkably small and negligible in comparison with those from both SR and MR SDCI methods. For distorted molecules, this error became somewhat more significant, approaching 1/4 of the MR SDCI one. Although the EN QDPT is inherently size-inconsistent [38], the deviations from additivity within the EN version of our approach were still much smaller than in SDCI methods, especially for the case of weak mixing of main and intermediate subspaces. Finally, we should note that [2/1] Padé resummation at least did not aggravate the size-inconsistency errors, slightly improving the additivity of the EN-based scheme.

Table VII. — *Deviations from additivity for energy estimates for two non-interacting Li₂ molecules ($\frac{1}{2}E(2\text{Li}_2) - E(\text{Li}_2)$, a.u.).*

Method	$r = 5.05$ a.u.	$r = 8$ a.u.
IH QDPT:		
MP, 3rd order	0.00020	0.00094
MP, [2/1] Pade	0.00021	0.00090
EN, 3rd order	0.00056	0.00222
EN, [2/1] Pade	0.00047	0.00178
SR CISD	0.00550	0.00637
MR CISD	0.00479	0.00377

4. Summary and conclusions.

A simple third-order intermediate-hamiltonian QDPT scheme is presented and applied to *ab initio* calculations of ground and several excited states of CH^+ , CH_2^+ and CH_2 . Both the Møller-Plesset and Epstein-Nesbet zero-order approximation are employed. The choice of extended model spaces as complete or nearly complete valence spaces necessitates the appearance of numerous intruder states which ruin the convergence of the conventional (non-shifted) QDPT expansions. Our method is shown to give an excellent approximation to full CI for both total energies and transition energies with very moderate computational efforts. In most cases the third order results exhibit a substantial improvement over second order, thus indicating a "practical convergency" of intermediate-Hamiltonian QDPT series. Third order corrections as well as estimates of higher-order terms from the modified [2/1] operator Padé approximants are of particular importance when the EN zero-order approximation is employed. The results obtained for several distorted geometries of CH_2 molecule prove the applicability of our method to potential energy surface calculations.

In contradistinction from the level shift method used in conventional effective Hamiltonian QDPT, the intermediate-Hamiltonian shift technique eliminates intruder states without introducing any additional perturbation. The importance of this feature is demonstrated by successful calculations on 2A_1 states of CH_2^+ , where the shifted effective Hamiltonian scheme [34] seems to diverge. The price to be paid is the partial loss of information on highly excited electronic states. However, this seems to be of no importance for the *ab initio* analysis of valence shell models because none of them are designed to describe *all* possible valence states of a molecule.

The non-additivity of the shift operators used in our scheme prohibits us from reaching strict size-consistency. Nevertheless, our calculations for two non-interacting molecules show that the deviations from size-consistency are fairly small, at least in comparison with those appearing in variational single- and multireference SDCI methods.

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